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Decomposition Reactions in the Flame Ionization Detector

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A computer simulation has been made of reactions postulated as occurring in the flame ionization detector, f.i.d. Upstream of the luminous zone, alkanes, alcohols and ethers decompose in an atmosphere of hydrogen to give methane. For each additive the calculated yield of methane equals the experimentally determined relative ionization yield. The response characteristics of the f.i.d. follow from this, provided that the additive decomposition and the ionization reaction occur in separate regions of the flame. For the very different response of an f.i.d. using carbon monoxide as fuel instead of hydrogen, the methane yield and the ionic yield are also equal.

Although the flame ionization detector, f.i.d., has been used in gas chromatography[1] as a sensitive and versatile detector of organic molecules for over twenty years, the chemical reactions which give it its particular electrical response are still not established. The f.i.d., as normally operated, is a hydrogen diffusion flame burning in air. The most detailed and satisfactory attempt to fit the experimental observations on the f.i.d. into current theories of hydrocarbon decomposition and of ionization in flames was that of Blades.[2] He proposed that the 'equal-per-carbon' response of the f.i.d. to hydrocarbon additives followed if all additives were converted to the same distribution of single-carbon hydrides prior to ionization or oxidation. Nicholson and Swingler[3] suggested that this distribution was set by the equilibrium of H_2, H, CH_4, CH_3, CH and C. The similar suggestion had been made by Hayhurst and Vince[4] that a number of phenomena in hydrogen flames, including ionization, could be correlated by assuming a series of stripping reactions

$$CH_n + H \rightarrow CH_{n-1} + H_2$$

of which one was the rate-determining step for production of CH. Blades[2] proposed that after the first reaction producing radicals the hydrocarbon chain was degraded by a series of H-atom cracking reactions such as

$$C_2H_5 + H \rightarrow 2CH_3.$$

The availability of a computer program[5] for simulating the kinetics of a number of coupled chemical reactions provided an opportunity for testing these postulates in a quantitative manner. A mechanism for the degradation process in the f.i.d. was set up using rate constants from the literature. In spite of uncertainties in our knowledge of some of these rate constants, the calculation gives an insight into which reactions contribute to the overall decomposition and which reactions are too slow to be relevant. It also shows whether equilibria can be attained in the time available. A mechanism involving methane production that does not require the equilibrium hypothesis will be shown to fit the facts adequately.

The experimentally observed f.i.d. relationships that must be deducible from a mechanistic theory are as follows.

(*a*) If Y_i is the ion yield per additive molecule, then Y_i is constant for additive concentrations from 10^{-9} to 10^{-2} of the concentration of the carrier gas.[6]

(*b*) If RY_i is the yield relative to methane taken as one, then RY_i equals the carbon number for hydrocarbon additives (the 'equal-per-carbon' response). Blades[2] showed that this relationship only holds if the additive is carried up to the flame in a gas stream containing hydrogen; this observation has recently[7] been questioned. The value for acetylene, $RY_i = 2.6$, is exceptional.[2, 6]

(*c*) For a carbon attached to a hetero-atom an 'effective carbon number' less than one can be determined.[6] RY_i for a molecule then equals the sum of the actual and effective carbon numbers, the latter being roughly transferable from molecule to molecule. Quantitative values ($C{=}O = 0$, $CH_3O = 0.3$ in dimethyl ether but zero for its homologues, $COH = 0.75$ and so on) must be reproduced by the mechanism.

(*d*) When carbon monoxide replaces hydrogen as fuel in an f.i.d., Y_i varies as the additive concentration at low concentrations and is constant at high concentrations.[8] Y_i for a carbon monoxide flame in the high-concentration region is *ca.* 0.08 of that for a hydrogen flame (from a comparison of the figures of McWilliam[8] and Sternberg *et al.*[6] for C_7H_{16}).

FLAME MODEL

A representative f.i.d. flame, as described in our earlier experiments,[3] had a blue luminous zone in the shape of a blunt-ended cylinder *ca.* 1.2 mm in diameter and 4 mm long. From the measurements of Ohline *et al.*[9] and of Mitchell *et al.*[10] on similar diffusion flames, a reasonable estimate of the temperature 0.1 mm inside the luminous zone is 1800 K. For a cold gas flow of 2 $cm^3\ s^{-1}$ the velocity of the gas as it passes through a 1 mm diameter × 4 mm long cylinder at 1800 K is *ca.* 1 $m\ s^{-1}$. The time for the gas to travel 0.1 mm is then 100 μs; the program was arranged to calculate the products formed in this time from various concentrations of the chosen additive reacting at 1800 K. The assumption is made that additive decomposition occurs in a hydrogen atmosphere in a region separate from that in which the ionizing and combustion reactions involving oxygen take place. Calcote[11] has shown that the maximum rate of ionization occurs downstream from the luminous zone where the temperature is also at a maximum. Mitchell *et al.*[10] give plots of [HCN] and [NO] as a function of position in a diffusion flame of methane burning in air. They show that [HCN] peaks at *ca.* 2 mm upstream of the luminous zone, where the temperature is 1400 K, whereas [NO] is almost separated from [HCN] and peaks at the temperature maximum, 2000 K, *ca.* 1 mm downstream from the luminous zone. In other words, the reducing and oxidizing regions of such flames are physically separate. The calculations given below are for the reducing region, and the half-lives obtained for the additive decomposition are a further justification for neglecting reactions between an additive and O or O_2.

COMPUTER PROGRAM

The program, developed by Davis,[5] uses Gear's algorithm for integrating a group of 'stiff' coupled differential equations. It has an option in which a system is considered at constant pressure with variable temperature and volume which corresponds reasonably to a flame. Preliminary runs showed that the compositions after 150 μs differed little regardless of whether a temperature rising in steps of 50 μs at each of 1600, 1700 and 1800 K or a fixed temperature of 1800 K was used, so the latter was chosen for convenience. The total gas concentration, [M], was taken as 4×10^{18} molecule cm^{-3}, of which 3×10^{18} molecule cm^{-3} was hydrogen. Concentrations of various additives from 10^{16} molecule cm^{-3} downwards were used. The program does not accept zeros so all free-radical and atom concentrations were set initially at 10^{-5} of the additive concentration. All reasonable reactions of the additive were written into the program, which calculated the concentrations of all the atoms, radicals and molecules as a function of time.

RATE CONSTANTS

The reactions and rate constants used for alkane pyrolysis [reactions (1)-(27)] are given in table 1. In general the rate constants used were taken from the review of Jensen and Jones.[12] This is a self-consistent set chosen for their applicability to flame temperatures. More recently Baulch and Duxbury[17] have recommended a slightly faster rate for reaction (3) but consider that its rate is falling off at *ca.* 10^{19} molecule cm^{-3} as it moves towards second-order kinetics. This makes little difference to the rate of

TABLE 1.—RATE CONSTANTS FOR THE PYROLYSIS OF PARAFFINS

$k = AT^n \exp(-E/RT)$, A/cm^3 molecule^{-1} s^{-1} or s^{-1}, T/K, $E/kJ\ mol^{-1}$

		forward			back			
		log A	n	E	log A	n	E	ref.
	initiation (unimolecular)							
1	$M+H_2 \rightleftharpoons H+H+M$	−5.10	−1	438	−29.52	−1	0	12
2	$M+CH_4 \rightleftharpoons CH_3+H+M$	5.70	−3	454	−20.70	−3	0	12
3	$C_2H_6 \rightleftharpoons CH_3+CH_3$	16.04	—	361	−11.00	—	−4.2	12
4	$C_2H_6 \rightleftharpoons C_2H_5+H$	16.04	—	403	—	—	—	—
5	$C_3H_8 \rightleftharpoons CH_3+C_2H_5$	16	—	343	−9.3	—	—	13
6	$C_3H_8 \rightleftharpoons C_3H_7+H$	16	—	393	−9.3	—	—	13
7	$C_4H_{10} \rightleftharpoons C_2H_5+C_2H_5$	15.30	—	323	−9.3	—	—	14
8	$C_4H_{10} \rightleftharpoons C_3H_7+CH_3$	15.30	—	356	−9.3	—	—	13
9	$C_4H_{10} \rightleftharpoons C_4H_9+H$	15.30	—	376	−9.3	—	—	13
10	$M+C_2H_4 \rightleftharpoons C_2H_3+H+M$	−6.22	—	411	−32	—	—	15
	initiation (bimolecular)							
11	$H+C_2H_5 \rightarrow CH_3+CH_3$	−9.3	—	0	—	—	—	16
12	$H_2+C_2H_2 \rightleftharpoons C_2H_3+H$	−11.28	—	269	−11.15	—	—	12
13	$H_2+C_2H_4 \rightarrow CH_3+CH_3$	−9.3	—	234	—	—	—	—
14	$H_2+C_3H_6 \rightarrow C_2H_5+CH_3$	−9.3	—	222	—	—	—	—
15	$C_2H_4+C_2H_4 \rightarrow C_2H_5+CH_3$	−8.96	—	268	—	—	—	15
	radical decomposition							
16	$M+C_2H_3 \rightarrow C_2H_2+H+M$	−8.92	—	126	−33	—	−40	12
17	$M+C_2H_5 \rightarrow C_2H_4+H+M$	−9.47	—	126	−32	—	—	15
18	$C_3H_7 \rightarrow C_3H_6+H$	13	—	173	−9.3	—	—	13
19	$C_3H_7 \rightarrow C_2H_4+CH_3$	13	—	139	−9.3	—	—	13
20	$C_4H_9 \rightarrow C_3H_6+CH_3$	13	—	137	—	—	—	13
21	$C_4H_9 \rightarrow C_2H_4+C_2H_5$	13	—	120	—	—	—	13
	hydrogen abstraction							
22	$H_2+CH_3 \rightleftharpoons CH_4+H$	−10.52	—	62.4	−9.15	—	62.4	12
23	$C_2H_6+CH_3 \rightleftharpoons CH_4+C_2H_5$	−24.04	4	34.6	−24.52	4	60.3	15
24	$H_2+C_2H_3 \rightleftharpoons C_2H_4+H$	−11.32	—	24	−10.52	—	29	12
25	$H_2+C_2H_5 \rightleftharpoons C_2H_6+H$	−16.64	2	38.6	−15.30	2	29	12
26	$H_2+C_3H_7 \rightleftharpoons C_3H_8+H$	−11	—	32	−10	—	32	—
27	$H_2+C_4H_9 \rightleftharpoons C_4H_{10}+H$	−11	—	32	−10	—	32	—
28	$M+HCO \rightleftharpoons CO+H+M$	−9.4	—	66	−32.7	—	7	12
29	$H_2+CO \rightleftharpoons HCO+H$	−10.85	—	400	−9.7	—	21	12

[a] Ref. (12) gives log $A_{25} = -17.64$ and log $A_{-25} = -16.30$. The values used here are at the upper limit of their error bounds.

reaction (3) at 1800 K. On the other hand, reaction (17) is in its transition region at this total gas concentration, so the second-order rate constant given by Koike and Gardner[15] is preferred. Uncertainties in knowledge of rate constants of hydrocarbons increase with increasing molecular weight; the values chosen here are rounded off values from the review by Benson and O'Neal.[13] They are slightly smaller than those given in a more recent review.[18] Provided that the rate constant for unimolecular decomposition is $> 7 \times 10^4$ s^{-1} (99.9% decomposition in 100 μs) the results obtained below are not sensitive to the value of this rate constant.

The back reactions between radicals given in table 1 are unimportant compared to the reactions of radicals with hydrogen. They only become significant when hydrogen is replaced by carbon monoxide, with which there is no equivalent metathetical reaction. Values of these rate constants were calculated from the equilibrium constants given by Jensen and Jones[12] or from those in the JANAF Tables,[19] or put equal to 5×10^{-10} cm^3 molecule^{-1} s^{-1}.

Decompositions involving the breaking of C—H bonds in hydrocarbons, reactions (4), (6) and (9), are rarely mentioned in the literature because they are usually overshadowed by reactions involving breaking of C—C bonds. If these rate constants are estimated by taking the same pre-exponential factor and correcting for the higher bond dissociation energy, D, then the C—H breaking rates are slower than the C—C breaking rates by $\exp[(D_{\mathrm{CH}}-D_{\mathrm{CC}})/\boldsymbol{R}T]$. This factor has a value of *ca.* 10 at 1800 K, and these reactions are in fact significant.

In table 2 are given rate constants for a mechanism with methanol and dimethyl ether as additives.

TABLE 2.—RATE CONSTANTS FOR THE PYROLYSIS OF CH_3OH AND CH_3OCH_3
$k = AT^n \exp(-E/\boldsymbol{R}T)$, A/cm^3 molecule^{-1} s^{-1} or s^{-1}, T/K, E/kJ mol^{-1}

		forward			back			
		log A	n	E	log A	n	E	ref.
	initiation							
30	$M+CH_3OH \rightleftharpoons CH_3+OH+M$	-5.3	—	335	-32	—	0	20
31	$M+CH_3OH \rightleftharpoons CH_3O+H+M$	-3	—	418	-32	—	0	—
32	$CH_3OCH_3 \rightleftharpoons CH_3O+CH_3$	15	—	318	-11.7	—	0	21
33	$CH_3OCH_3 \rightleftharpoons CH_2OCH_3+H$	15	—	418	-11.7	—	0	—
	radical decomposition							
34	$M+CH_3O \rightleftharpoons CH_2O+H+M$	-10	—	121	-11.7	—	0	20
35	$M+CH_2OCH_3 \rightleftharpoons CH_2O+CH_3+M$	-10.4	—	60	-11.7	—	0	21
	hydrogen abstraction							
36	$OH+CH_3OH \rightleftharpoons CH_3O+H_2O$	-11.18	—	8.4	-9.3	—	71	20
37	$CH_3+CH_3OCH_3 \rightleftharpoons CH_2OCH_3+CH_4$	-10.3	—	63	-9.3	—	75	20
38	$OH+H_2 \rightleftharpoons H_2O+H$	-14.72	1.3	15	-14.08	1.3	77.6	12
39	$CH_3O+H_2 \rightleftharpoons CH_3OH+H$	-9.3	—	48	-10.7	—	29	—
40	$CH_2OCH_3+H_2 \rightleftharpoons CH_3OCH_3+H$	-9.3	—	20	-9.3	—	16	—
41	$CH_3+CH_3OH \rightleftharpoons CH_3O+CH_4$	-12.52	—	41	-11.2	—	55.6	22

RESULTS

ETHANE, PROPANE AND BUTANE

Fig. 1 shows the products formed as a function of time when 10^9 molecule cm^{-3} of C_2H_6 is taken as the initial concentration of additive in the scheme of table 1.

This figure shows that: (i) The major molecular product is CH_4, and in 10 μs it has reached a limit set by the amount of C_2H_6 initially present. Little change in products occurs between 10 and 100 μs. (ii) For reactions (1) and (-1) the equilibrium value

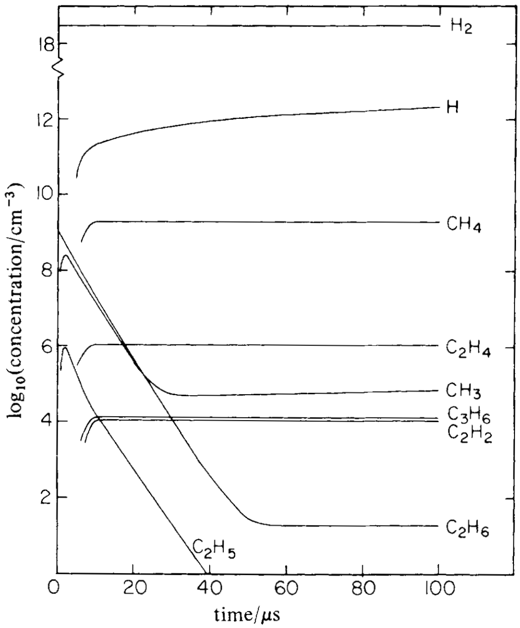

FIG. 1.—Plots of the logarithm of the concentrations of the products from 10^9 molecule cm^{-3} of C_2H_6 as additive against time at 1800 K. Hydrogen flame.

of [H] (1.25×10^{15} atoms cm^{-3} at 1800 K) has not been reached. Dissociation of H_2 is negligible. (iii) C_2H_4 is present to *ca.* 0.05% of the CH_4. Its amount is decreasing but so slowly as not to be visible on this scale. The amount is 10^5 times greater than it would be if the equilibrium

$$C_2H_4 + 2H_2 \rightleftharpoons 2CH_4$$

had been established. (iv) Reactions (22) and (−22) are almost in equilibrium: $[CH_3][H_2]/[CH_4][H] = 47$, whereas the equilibrium value is 23. Other products have reached 'steady states' that are not equilibria.

Fig. 2 gives similar plots for an initial ethane concentration of 10^{15} molecule cm^{-3}. Once again CH_4 is the main product, although the relative proportions of the minor products have changed. [H] is higher than the equilibrium value, and equals [CH_4] throughout. The equilibrium of reactions (22) and (−22) is established. [C_2H_4] at 100 μs is now 0.4% of [CH_4]. Reactions (3) and (−3) are almost in equilibrium.

If initial concentrations of propane or butane are substituted for ethane into the scheme of table 1, the general shape of the concentration against time curves remains the same and methane remains the dominant product. Product concentrations after 100 μs for equivalent concentrations of the first four alkanes are given in table 3.

The postulate that every alkane produces the same distribution of minor products is wrong, but the quantities of minor products are so small relative to the quantities of methane that their effect on the yield of methane is negligible.

Fig. 3 is a log–log plot of the concentrations of some of the products against the initial additive concentration. This particular plot is for C_3H_8 additive, but the plots are the same for C_2H_6 and C_4H_{10} except for the absolute values of the ordinate. Over a dynamic range of at least 10^7, [CH_4] is linear with initial additive concentration,

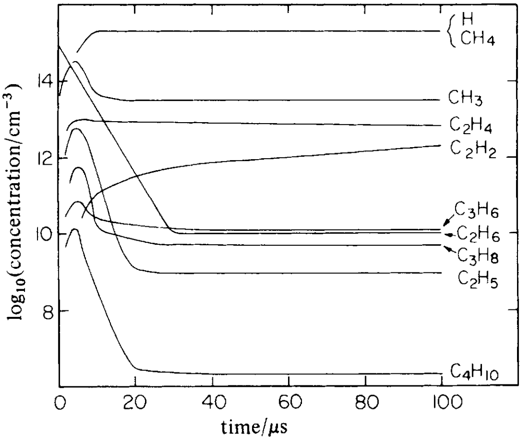

FIG. 2.—Plots of the logarithm of the concentrations of the products from 10^{15} molecule cm^{-3} of C_2H_6 as additive against time at 1800 K. Hydrogen flame.

TABLE 3.—DECOMPOSITION PRODUCTS AFTER 100 μs FOR PARAFFIN ADDITIVES

additive	initial concentration /10^{14} molecule cm^{-3}	product after 100 μs concentration/molecule cm^{-3}						
		CH_4	H	CH_3	C_2H_4	C_2H_2	C_3H_6	C_2H_5
C_4H_{10}	1	3.7×10^{14}	5.7×10^{14}	1.6×10^{12}	1.5×10^{13}	1.0×10^{12}	4.4×10^{9}	3.1×10^{7}
C_3H_8	1.3	3.8×10^{14}	5.4×10^{14}	4.0×10^{12}	6.8×10^{12}	3.2×10^{12}	1.6×10^{9}	9.3×10^{6}
C_2H_6	2	4.0×10^{14}	4.2×10^{14}	5.3×10^{11}	3.8×10^{11}	1.2×10^{11}	6.2×10^{8}	2.7×10^{5}
CH_4	4	4.0×10^{14}	4.0×10^{12}	1.9×10^{10}	3.5×10^{9}	1.3×10^{9}	1.1×10^{9}	4.0×10^{4}

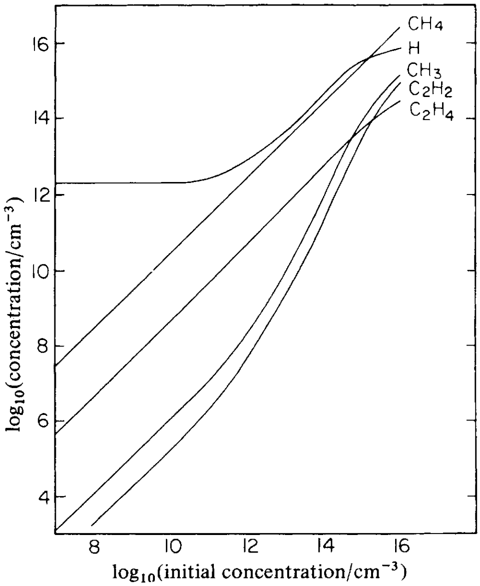

FIG. 3.—Log–log plot of concentration of products after 100 μs against initial concentration of additive, C_3H_8, at 1800 K. Hydrogen flame.

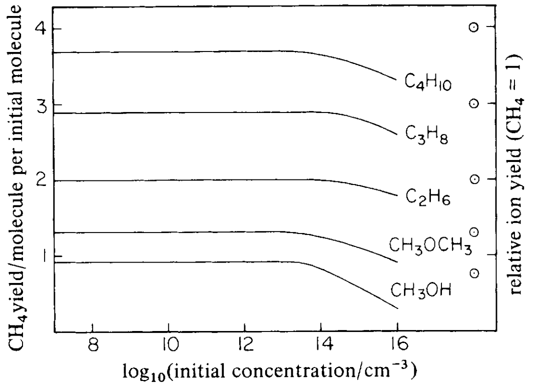

FIG. 4.—CH_4 yield, molecule at 100 μs per initial additive molecule plotted against the logarithm of the initial concentration. The circles give the ion yield, ions per additive molecule relative to $CH_4 = 1$. Hydrogen flame.

i.e. its yield per additive molecule, Y_{CH_4}, is constant, and as shown in fig. 4 this yield is almost equal to the carbon number of the additive. Methane is the only product for which this is true, and neither relationship holds for methyl radical concentration. Rather, over the range 10^{12}-10^{14} molecule cm^{-3} of additive the slope of the log [CH_3] line is 2. The point (*ca.* 10^{12} molecule cm^{-3}) where this curve steepens corresponds to the point where the [H] curve approaches the [CH_4] straight line. At this point also the equilibrium of reactions (22) and (−22) is established, *i.e.* $[CH_3] = [CH_4][H]/K_{22}[H_2]$, and the square law follows since both [CH_4] and [H] vary as the initial additive concentration.

The only liberty taken in selecting rate constants was to put k_{25} at the upper limit of the range given in ref. (12). Y_{CH_4} is sensitive to the ratio of the rates of reaction (25) to reaction (7) and, if this is reduced by a factor of 10, Y_{CH_4} for C_4H_{10} is reduced to 3.2 although the yield from C_3H_8 or C_2H_6 is barely altered.

CARBON MONOXIDE FLAME

Reactions in a carbon monoxide flame are simulated by the reactions for alkanes plus reactions (28) and (29) with the initial H_2 replaced by CO. The distribution of products, fig. 5, is now quite different (*cf.* fig. 1). CH_3 is the major product, CH_4 a minor one and it is the equilibrium of reactions (3) and (−3) which is reached. In fig. 6 a log–log plot of the products against initial additive concentration also demonstrates a reversal since [CH_3] is linear with additive at low additive concentrations, whereas over the range 10^{11}-10^{14} molecules of additive per cm^3, [CH_4] varies as the square of the initial additive concentration. Thus for both flames it is the methane yield which parallels the RY_i behaviour given in the introduction under (*a*), (*b*) and (*d*). In the CO flame at low concentrations [H_2] is also proportional to the square of the additive concentration, but once the absolute amount of hydrogen becomes appreciable the system moves towards that of a hydrogen flame, the [CH_4] and [CH_3] curves cross and the [CH_4] tends towards being proportional to the first power of the additive concentration. This behaviour is also paralleled by RY_i in CO flames,[8] although the changeover occurs at a lower concentration than in the model system. The ratio of the methane yields at initial [C_2H_6] = 10^{15} molecule cm^{-3} in CO and H_2 is 0.025, whereas the corresponding ratio of ion yields is 0.08. Agreement is fair when one considers that experimental data on CO flames are scarce and that there

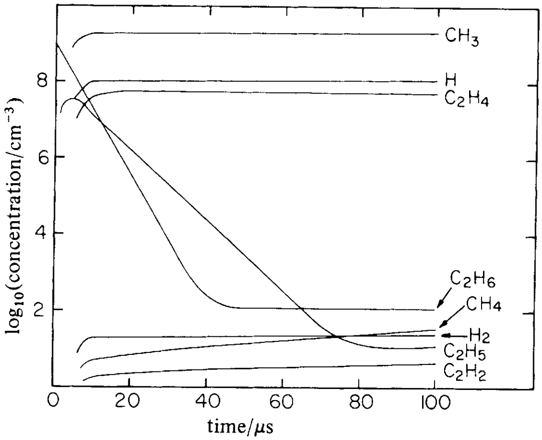

FIG. 5.—Plots of the logarithm of the concentrations of products from 10^9 molecule cm^{-3} of C_2H_6 as additive against time at 1800 K. Carbon monoxide flame.

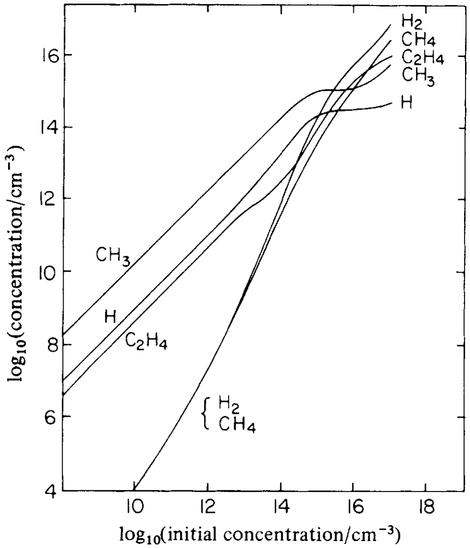

FIG. 6.—Log–log plot of concentration of products after 100 μs against initial concentration of additive, C_2H_6, at 1800 K. Carbon monoxide flame.

are doubts[8] about the purity of the carbon monoxide used in some of the published experiments.

OXYGEN-CONTAINING MOLECULES

The reaction

$$CH + O \rightarrow HCO$$

is so exothermic that there is enough energy available to ionize HCO. Conversely, the reactions reducing a carbonyl group to CH are so endothermic, and accordingly slow, that a carbonyl group gives zero ionic response in the f.i.d. It follows that any reaction of the O-containing molecule that produces a carbonyl group will lower the value of RY_i if it is fast enough to compete with the reactions producing ions. If, as indicated above, CH_4 production is an essential step in the path to ion production, this possibility can be further tested by seeing whether Y_{CH_4} is lower than the carbon number for dimethyl ether and methanol. Formaldehyde is the obvious carbonyl compound that could be formed from these additives. The question is whether its rate of formation is comparable with that of CH_4 formation. These decompositions have been modelled by adding the reactions of table 2 to reactions (1)-(4), (11), (13), (17), (22), (23) and (25) of table 1; the rate constant values of table 2 are more uncertain than those of table 1.

DIMETHYL ETHER

The yields of methane, Y_{CH_4}, for CH_3OCH_3 over a range of additive concentrations are shown in fig. 4. The value $k_{34} = 1 \times 10^{-10} \exp(-121\,000/\boldsymbol{RT})$ gives $Y_{CH_4} = 1.3$ in exact agreement with RY_i for CH_3OCH_3.[2] For all concentrations, the sum of Y_{CH_4} and Y_{H_2CO} is two. The agreement is only of limited significance since Y_{CH_4} is sensitive to the value of k_{34}; specifically, Y_{CH_4} is reduced to 1 by increasing k_{34} by a factor of 40. However, this sensitivity means that a slight increase in the rate constants of the equivalent of k_{34} (*e.g.* $CH_3CH_2O \rightarrow CH_3 + H_2CO$ for diethyl ether) would account for the zero RY_i of the ether group in all ethers other than dimethyl ether.[6]

METHANOL

For CH_3OH decomposition, CH_3O has been used to represent the two radicals CH_3O and H_2COH, since no quantitative data are available to determine any difference in their reactivities. The hydrogen abstraction reactions, (36), (−39) and (41), are not fast enough to produce H_2CO *via* CH_3O in appreciable quantities in the times considered here.

Accordingly, reaction (31) is postulated with a rate making it competitive with reaction (30). The Y_{CH_4} value calculated is then 0.93. This is higher than the RY_i value of 0.75 given by Sternberg *et al.*[6] However, Y_{CH_4} falls off at high additive concentrations more sharply than the yield from alkanes (fig. 4) and, since the measurements of Sternberg *et al.* were made over the range 10^{13}-10^{15} molecule cm^{-3}, the discrepancy is not large. As for CH_3OCH_3, the sum of Y_{CH_4} and Y_{H_2CO} equals the carbon number of the additive.

ETHYLENE AND ACETYLENE

In an earlier paper[3] we assumed that ethylene and acetylene would be reduced to alkanes by the excess of hydrogen present sufficiently rapidly for degradation to methane to occur. The calculations of the present paper make this unlikely, but the values chosen for the rate constants are uncertain. The only measurements of gas-phase hydrogenation date from the 1930s, of Pease[23] on C_2H_4 and Taylor and van Hook[24] on C_2H_2. For such chain reactions it is possible to calculate the rate constant for the initiation reaction from the overall rate of the reaction; Semenoff[25] gives such a calculation for Pease's measurements. Even if the assumed mechanism is correct, the initiation reaction contributes only a small fraction to the overall reaction and cannot be specified very accurately. Reactions (11)-(15), grouped under the heading of 'Bimolecular Initiation' have been assigned rate constants at the upper limit of what seems reasonable in an endeavour to find a reaction path from unsaturated to saturated that could be significant in 100 μs. All are inadequate and their omission, along with reaction (10) and all reactions involving C_2H_2 and C_2H_3, makes a negligible alteration to the calculations described above for the alkanes. The fastest reaction removing C_2H_4 is reaction (10), and its half-life is 0.36 s at 1800 K and 2.3×10^{-3} s at 2200 K, which is about the highest temperature reached in f.i.d. flames. On present knowledge of rate constants, C_2H_4 and C_2H_2 must be regarded as exceptions which do not degrade to CH_4 within 100 μs at 1800 K as do alkanes, alcohols and ethers.

METHANE

Methane, like C_2H_4 and C_2H_2, decomposes by breaking a C—H bond which is stronger than the C—C bonds in its homologues. The lifetime of CH_4 for decomposition by reaction (2) is 4.3×10^{-2} s at 1800 K and 3.9×10^{-4} s at 2200 K. CH_4, C_2H_4 and C_2H_2 are unique among the gases considered here in that their lifetimes are long with respect to the time-scale used in the calculations. A calculation of products after 100 μs is given in table 3. For the same final amount of CH_4 the amounts of minor products are markedly different for CH_4 itself than for its homologues decomposing to CH_4.

DISCUSSION

The calculations given here were planned to give quantitative expression to the mechanism given in a previous paper,[3] which was itself an extension of the mechanism given by Blades.[2] Two assumptions made there[3] are shown here to be wrong. The first is that equilibrium is reached in the $H_2 \rightleftharpoons 2H$ reaction [reactions (1) and (−1)]. In 100 μs, [H] is above its equilibrium value at high additive concentrations and below it at low concentrations. The equilibrium

$$CH_3 + H_2 \rightleftharpoons CH_4 + H$$

is only attained at the high end of the additive concentration range. The calculations made here give concentrations reached after 100 μs, and whether these are equilibrium values or not is irrelevant. The second, made originally by Blades[2] that 'all additives give the same distribution of single carbon hydrides before ionization' is not quite correct. All additives give CH_4 as a major product, while the variable amounts of minor products make a negligible contribution to the decomposition. It has been shown that Y_{CH_4} from C_2H_6, C_3H_8 and C_4H_{10} parallels the relative ionization yield in the usual f.i.d. (H_2 flame) in its major characteristics; the constancy with additive concentration, the wide range of this constancy and its equality to the carbon number. Considerable alterations to the rate constants given in table 1 would be needed to cause a departure from this parallelism. In the f.i.d. with CO as fuel, $\boldsymbol{R}Y_i$ is linear with concentration over a small range and then becomes almost constant; this is also the behaviour of Y_{CH_4}. Although the rate constants needed are less accurately known, the calculation also correlates Y_{CH_4} from oxygen-containing compounds with the effective carbon numbers in the f.i.d. of the COH and CH_3O groups.

A complete explanation of the f.i.d. relationships then requires a mechanism yielding ions in amounts proportional to CH_4 concentration. Experimentally this was established by Peeters *et al.*[26] for a premixed flame with $H_2 : O_2 = 7:3$ and it holds for CH_4 in the f.i.d. diffusion flame. A surprising result of the calculations given above is that while $[CH_4]$ is linear with additive concentration over the whole range over which ionization is linear, $[CH_3]$ is at first linear, then follows a square law and finally requires an intermediate exponent as the additive concentration rises (fig. 3). This suggests that the reaction path giving ionization (whether *via* CH or in any other way) proceeds from CH_4 without passing through CH_3. A possible reaction by-passing CH_3 formation is

$$CH_4 \rightarrow CH_2 + H_2$$

for which Chen *et al.*[27] give a rate constant of $6.3 \times 10^{14} \exp(-474000/\boldsymbol{R}T)\ s^{-1}$, stating that this is probably a maximum value. We used a value of one quarter of this in a simulation of the reactions of the single-carbon hydrides with H, H_2 and C and found that [CH_2], [CH] and [C] were proportional to the initial [CH_4] while [CH_3] was proportional to the square of the initial [CH_4]. No more is claimed for this calculation than that it provides a possible mechanism, since most of the rate constants used were estimated.

This calculation also shows that the hydrogen-atom cracking mechanism postulated by Blades is relatively unimportant. For example, in the reaction plotted in fig. 2 the rate of removal of C_2H_5 by atom cracking, reaction (11), is 10^6 [C_2H_5] molecule cm^{-3} s^{-1}, whereas by hydrogen abstraction, reaction (25), it is 1.7×10^7 [C_2H_5] molecule cm^{-3} s^{-1}. At lower additive concentration reaction (11) is even slower, 10^2 [C_2H_5] molecule cm^{-3} s^{-1} for the reaction of fig. 1, whereas k_{25} [H_2] does not change with additive concentration. The calculations show that it is reactions with the hydrogen *molecule* that are important and that alkane decomposition is complete before an appreciable amount of hydrogen has dissociated. This high concentration of hydrogen, in suppressing radical–radical reactions, is essential to give total conversion to the single-carbon compound, CH_4. Recently Wagner *et al.*[7] have examined the response of alkanes in the hydrogen atmosphere flame ionization detector, h.a.f.i.d, in which the additive is carried in an oxygen stream, in the inner of two concentric jets, to burn in an atmosphere of hydrogen. They observed an equal-per-carbon response, which seems to be in direct contradiction to measurements of Blades,[2] and state that 'an explanation unifying the results reported in this study and in that of Blades remains unclear'. They also state that 'if only one mechanism is to be proposed as the origin of the equal-per-carbon response it must operate in both hydrogen-rich and oxygen-rich environments'. The mechanism involving CH_4 formation advanced here cannot operate in an oxygen-rich flame and a postulate that more than one mechanism exists seems more likely. A difference worth noting is that while the response and methane formation are linear over seven orders of additive concentration in the f.i.d., the h.a.f.i.d. response is only linear over two. Response-per-carbon is only meaningful in the linear region. Additive decomposition in oxygen atmosphere might resemble the carbon monoxide experiments modelled in this paper, where methane formation exhibits both linear and square-law variations with concentrations.

Since the mechanism involving CH_4 production cannot be true for C_2H_4 and C_2H_2 an *ad hoc* postulate must be made that some other route to ionization is available for these two gases. Blades pointed out the anomalous position of C_2H_2 referring to 'the embarrassing situation of basing the mechanism of ion formation on work on C_2H_2, the very compound for which there is evidence of unique behaviour'. He emphasized that C_2H_2 catalyses H-atom recombination[28] rather than being itself reduced, that ionizing reactions other than CH + O could not be ruled out with certainty, and that a $C_2H + O_2^*$ ionizing reaction might be peculiar to C_2H_2. Later, Blades[29] compared ionization rate with CH emission rate and showed that their ratio was higher for C_2H_2, C_2H_4 and CH_4 than for other alkanes. He argued that this required an additional ionization reaction to the generally accepted reaction *via* CH. The most detailed study of the chem-ionization of C_2H_2 by O atoms, that of Vinckier *et al.*,[30] goes no further than saying that 'an intermediate' gives HCO^+, either in a reaction with O or *via* CH which reacts with another O atom. These observations and the still unexplained RY_i value of 2.6 for acetylene are not inconsistent with the view that acetylene is a special case. It would seem that C_2H_4 is also, although this has not been apparent since its RY_i value of 1.98 fits into the normal pattern. The differences between CH_4 as additive and CH_4 produced from higher alkanes might be associated with the differences in minor products shown in table 3.

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