Kinetics of Soot Cluster Formation at High Temperatures*

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The soot formation during combustion is described by a theory based on cluster kinetics. Kinetic calculations in which carbon vapors ($C_1 - C_5$) and polyacetylenes are assumed to be the collision partners for cluster reactions support the formation by soot via soot clusters at higher temperatures. The prediction of the proposed theory agrees well with both the bell-shaped temperature dependence of soot yield and the rapid soot formation as observed from shock-tube experiments. It is also shown that the small clusters are mainly generated via C_2H , and they grow into large clusters by reaction with carbon vapors at moderately high temperatures, while they are decomposed into carbon vapors at very high temperatures. Furthermore, the effects of pressure and heterogeneous nuclei such as condensed PAHs on soot formation are discussed.

Key Words: Combustion, Combustion Products, Soot Formation, Carbon Cluster, Chemical Reaction, Homogeneous Nucleation

1. Introduction

Nucleation and particle growth mechanisms significantly affect the rate of soot formation during combustion. Many previous studies have dealt with heterogeneous nucleation, based on the assumption that intermediate products such as radical fragments and polynuclear aromatic hydrocarbons (PAHs) play an essential role in the nucleation step. Those studies mainly addressed the behavior and reaction rates of such intermediate products, because nucleation is the rate-controlling step in this scheme. Recently, some detailed chemical kinetic models along this line have been developed^{(1),(2)} and predicted, with some success, the formation of PAHs in flames⁽³⁾. At present, however, these models cannot fully explain the rapid condensation into large soot particles consisting of as

many as $10^6 - 10^{12}$ carbon atoms.

Previously, some of the authors of this paper proposed a theory based on homogeneous nucleation using a kinetic cluster model^{(4),(5)}. In that study, the likelihood of homogeneous nucleation was assessed in depth from a thermodynamic aspect, taking the Gibbs free energy of each intermediate product into consideration. It was suggested that at high temperatures soot is formed by homogeneous nucleation from carbon vapors through carbon clusters. This theory described well a series of soot-formation steps consisting of fuel decomposition, nucleation, particle growth and soot oxidation. Also predicted was the bell-shaped profile of soot yield against temperature, observed in shock-tube experiments of Frenklach et al.⁽³⁾ In this theory, however, instead of taking full chemical kinetics into account, the rate-controlled partial equilibrium was assumed to hold for elementary reactions such as those of colliding partners ($C_1 - C_5$). For this reason, the predicted concentrations of carbon vapors are not very accurate in the earlier stages of the soot-forming reaction. Therefore, we developed a full kinetic theory for soot formation as the next step.

* Received 17th December, 1992. Paper No. 91-1519

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The present paper reports on the improved theory which includes detailed chemical reactions not only for gaseous species but also for carbon vapors; also included is the cluster reaction via C_2H which might be significant at intermediate temperatures. The predicted results support well the sooting pathways via carbon clusters. There is also detailed discussion on the rate-determining step of soot formation and temperature dependence of the soot yield, based on a sensitivity analysis. Furthermore, the effects of pressure and temperature history on soot formation are discussed.

2. Basic Concept and Calculation Method

This theory assumes clusters of pure carbon ranging from monomer to 10^{12} -mer. Many previous studies showed that particulates sampled from flames contain younger soot particles having considerable amounts of hydrogen. It is possible to extend the present theory to describe polyacetylene clusters that contain hydrogen, but such treatment was not introduced in this study, because soot formation in the case where the mixture is suddenly heated to high temperatures, e.g., shock-heated pyrolysis, will occur after dehydrogenation of the fuel fragments, and it is not certain if hydrogen is an essential member of the crystalline-structured soot particle, unlike the soot formed in ordinary flames.

The following reactions are assumed to hold for growth and oxidation of n -mer C_n :

where M is the third body that may remove energy and C_i the colliding partner whose class i ranges from 1 to 5. Clusters of 6-mer or more do not act as the partner because of the negligible probability of collision. All reactions of cluster oxidation other than that by OH are ignored in view of their negligible contribution in reactions of mixture fuel-rich enough to generate soot.

Rate constants for cluster reactions are derived based on Bauer and Frurip's self-consistent kinetic model (SCKM)⁽⁶⁾. This model assumes that the third body removes the surplus energy at each collision, thereby stabilizing the product of $(i+n)$ -mer in reaction (1). The rate constant of this reaction is given by assuming the Lennard-Jones potential which is determined by the physical sizes and enthalpies of formation of colliding pairs of n -mers and i -mers and of the product $(n+i)$ -mers. The reverse rate for n -mer reaction may be calculated using equilibrium constants obtained also from SCKM. The details of the Gibbs free energies of the clusters have been reported elsewhere^{(4),(5)}.

Generally speaking, the Gibbs free energy of a

small cluster is strongly dependent on the bonding structure of its surface layer and may vary from class to class. However, the scatter would decrease as the cluster core, whose structure changes little from class to class, becomes predominant with an increase of cluster class. Therefore, the Gibbs free energy was simply determined by SCKM, which gives continuously changing values with cluster class.

From the thermochemical point of view, polyacetylenes such as C_2H_2 , C_4H_2 , C_6H_2 and also polyacetylene radicals such as C_2H , C_3H , C_4H are the likely condensable species that act as colliding partners during clustering at higher temperatures⁽⁹⁾. For this reason, reactions between carbon clusters and such polyacetylenes should also be taken into account. In the reaction between C_n and C_iH_j , the hydrogen atoms should be cleaved off from C_iH_j to stabilize the product C_{n+i} , because C_{n+i} has a lower enthalpy of formation than C_n on a mass basis. In such reactions, polyacetylene radicals are most appropriate as the condensable species, two H atoms are unlikely to be abstracted simultaneously and radical reactions are fast enough which explains the rapid clustering. Among polyacetylene radicals, C_2H can be observed in many flames and is energetically more stable than others. Jensen⁽⁷⁾ assumed C_2H as being the primary molecule in his theory for soot formation. Thus, we used the same assumption that C_2H is condensable and reacts with a cluster.

The rate constants of reaction (3) are not well established and were estimated from the rate constants of similar reactions as follows⁽⁸⁾.

where A and E_a are the pre-exponential factor and the activation energy, respectively, in units of kcal, mol, cm^3 and s. The exponent n is dimensionless. Each expressed radical reaction has zero activation energy and a pre-exponential factor that is equal to the collision frequency multiplied by an almost constant steric factor. Taking these facts into consideration, we may assume that reaction (3) has zero activation energy. Thus, the rate constants of reaction (3) were determined based on a simple molecular kinetic theory as follows:

$$A = P\pi(\eta_{C_n} + \eta_{C_2H})^2(8kT/\pi\mu)^{1/2} \quad (7)$$

where η_{C_n} and η_{C_2H} are the hard-sphere radii of C_n and C_2H , respectively, μ the reduced molecular weight of n -mer and C_2H , k the Boltzmann constant, and P the steric factor. The reverse rate constants k^- of reaction (3) were obtained from the equilibrium

Table 1 Forward rate constants of elementary reactions

No.	Reaction	$k = AT^n \exp(-E/RT)$		
		A ($\text{cm}^3, \text{mol}, \text{s}$)	n	E (kcalmol^{-1})
1	$\text{H}_2 + \text{OH} = \text{H}_2\text{O} + \text{H}$	$1.20\text{E}+09$	1.3	3.63
2	$\text{H}_2 + \text{O} = \text{H} + \text{OH}$	$1.50\text{E}+07$	2.0	7.55
3	$\text{H} + \text{O}_2 = \text{O} + \text{OH}$	$1.20\text{E}+17$	-0.9	16.62
4	$\text{H} + \text{H} + \text{M} = \text{H}_2 + \text{M}$	$9.00\text{E}+16$	-0.6	0.0
5	$\text{H} + \text{OH} + \text{M} = \text{H}_2\text{O} + \text{M}$	$2.20\text{E}+22$	-2.0	0.0
6	$\text{H} + \text{HO}_2 = \text{OH} + \text{OH}$	$1.50\text{E}+14$	0.0	1.00
7	$\text{H} + \text{HO}_2 = \text{H}_2 + \text{O}_2$	$2.50\text{E}+13$	0.0	0.69
8	$\text{H} + \text{HO}_2 = \text{H}_2 + \text{O}$	$1.00\text{E}+13$	0.0	1.07
9	$\text{H} + \text{O}_2 + \text{M} = \text{HO}_2 + \text{M}$	$2.30\text{E}+18$	-0.8	0.0
10	$\text{HO}_2 + \text{OH} = \text{H}_2\text{O} + \text{O}_2$	$1.50\text{E}+13$	0.0	0.0
11	$\text{HO}_2 + \text{O} = \text{O}_2 + \text{OH}$	$2.00\text{E}+13$	0.0	0.0
12	$\text{HO}_2 + \text{HO}_2 = \text{H}_2\text{O}_2 + \text{O}_2$	$2.00\text{E}+12$	0.0	0.0
13	$\text{H}_2\text{O}_2 + \text{H} = \text{H}_2\text{O} + \text{H}_2$	$1.70\text{E}+12$	0.0	3.75
14	$\text{H}_2\text{O}_2 + \text{OH} = \text{H}_2\text{O} + \text{HO}_2$	$1.00\text{E}+13$	0.0	1.80
15	$\text{H}_2\text{O}_2 + \text{M} = \text{OH} + \text{OH} + \text{M}$	$1.20\text{E}+17$	0.0	45.50
16	$\text{OH} + \text{OH} = \text{H}_2\text{O} + \text{O}$	$1.50\text{E}+09$	1.1	0.0
17	$\text{CO} + \text{OH} = \text{CO}_2 + \text{H}$	$1.50\text{E}+07$	1.3	-0.77
18	$\text{CO} + \text{HO}_2 = \text{CO}_2 + \text{OH}$	$1.50\text{E}+14$	0.0	23.65
19	$\text{CO}_2 + \text{O} = \text{CO} + \text{O}_2$	$2.80\text{E}+12$	0.0	43.83
20	$\text{C}_2\text{H}_3 + \text{O}_2 = \text{HCO} + \text{CH}_2\text{O}$	$4.00\text{E}+12$	0.0	-0.25
21	$\text{CH}_2\text{O} + \text{H} = \text{HCO} + \text{H}_2$	$1.00\text{E}+14$	0.0	4.95
22	$\text{CH}_2\text{O} + \text{OH} = \text{HCO} + \text{H}_2\text{O}$	$1.80\text{E}+13$	0.0	0.44
23	$\text{CH}_2\text{O} + \text{O} = \text{HCO} + \text{OH}$	$6.00\text{E}+13$	0.0	3.80
24	$\text{CH}_2\text{O} + \text{HO}_2 = \text{HCO} + \text{H}_2\text{O}_2$	$1.00\text{E}+09$	0.0	0.0
25	$\text{CH}_2\text{O} + \text{CH}_3 = \text{CH}_4 + \text{HCO}$	$1.00\text{E}+11$	0.0	6.00
26	$\text{CH}_2\text{O} + \text{M} = \text{HCO} + \text{H} + \text{M}$	$5.00\text{E}+16$	0.0	76.48
27	$\text{HCO} + \text{M} = \text{H} + \text{CO} + \text{M}$	$2.50\text{E}+14$	0.0	16.80
28	$\text{HCO} + \text{H} = \text{CO} + \text{H}_2$	$7.20\text{E}+13$	0.0	0.0
29	$\text{HCO} + \text{OH} = \text{CO} + \text{H}_2\text{O}$	$5.00\text{E}+13$	0.0	0.0
30	$\text{HCO} + \text{O}_2 = \text{CO} + \text{HO}_2$	$5.00\text{E}+11$	0.5	0.83
31	$\text{HCO} + \text{O} = \text{CO} + \text{OH}$	$3.00\text{E}+13$	0.0	0.0
32	$\text{HCO} + \text{O} = \text{CO}_2 + \text{H}$	$3.00\text{E}+13$	0.0	0.0
33	$\text{HCO} + \text{CH}_3 = \text{CO} + \text{CH}_4$	$3.00\text{E}+11$	0.5	0.0
34	$\text{CH}_2\text{CO} + \text{OH} = \text{CH}_2\text{O} + \text{HCO}$	$1.00\text{E}+13$	0.0	0.0
35	$\text{CH}_2\text{CO} + \text{H} = \text{CH}_3 + \text{CO}$	$7.00\text{E}+12$	0.0	3.01
36	$\text{CH}_2\text{CO} + \text{O} = \text{HCO} + \text{HCO}$	$2.00\text{E}+13$	0.0	2.29
37	$\text{CH}_2\text{CO} + \text{M} = \text{CH}_2 + \text{CO} + \text{M}$	$3.60\text{E}+15$	0.0	59.30
38	$\text{CH}_4 = \text{CH}_3 + \text{H} \text{ (pd)}$	$1.10\text{E}+33$	-5.9	105.15
39	$\text{CH}_4 + \text{H} = \text{CH}_3 + \text{H}_2$	$7.20\text{E}+14$	0.0	15.10
40	$\text{CH}_4 + \text{O} = \text{CH}_3 + \text{OH}$	$6.90\text{E}+08$	1.6	8.54
41	$\text{CH}_4 + \text{OH} = \text{CH}_3 + \text{H}_2\text{O}$	$5.70\text{E}+06$	2.0	2.64
42	$\text{CH}_4 + \text{CH}_2 = \text{CH}_3 + \text{CH}_3$	$1.00\text{E}+13$	0.0	0.0
43	$\text{CH}_4 + \text{HO}_2 = \text{CH}_3 + \text{H}_2\text{O}_2$	$2.00\text{E}+13$	0.0	18.00
44	$\text{CH}_3 + \text{CH}_3 = \text{C}_2\text{H}_6 + \text{H}$	$7.80\text{E}+11$	0.0	13.04
45	$\text{CH}_3 + \text{O}_2 = \text{CH}_2\text{O} + \text{OH}$	$1.50\text{E}+13$	0.0	28.70
46	$\text{CH}_3 + \text{H} = \text{CH}_2 + \text{H}_2$	$7.20\text{E}+14$	0.0	15.10
47	$\text{CH}_3 + \text{O} = \text{CH}_2\text{O} + \text{H}$	$8.40\text{E}+13$	0.0	0.0
48	$\text{CH}_3 + \text{CH}_3 = \text{C}_2\text{H}_4 + \text{H}_2$	$1.00\text{E}+16$	0.0	31.79
49	$\text{CH}_3 + \text{CH}_2 = \text{C}_2\text{H}_4 + \text{H}$	$2.00\text{E}+13$	0.0	0.0
50	$\text{CH}_2 + \text{O}_2 = \text{CO} + \text{OH} + \text{H}$	$1.30\text{E}+13$	0.0	1.45
51	$\text{C}_2\text{H}_6 + \text{H} = \text{C}_2\text{H}_5 + \text{H}_2$	$1.30\text{E}+14$	0.0	9.37
52	$\text{C}_2\text{H}_6 + \text{O} = \text{C}_2\text{H}_5 + \text{OH}$	$1.80\text{E}+13$	0.0	6.10
53	$\text{C}_2\text{H}_6 + \text{OH} = \text{C}_2\text{H}_5 + \text{H}_2\text{O}$	$6.30\text{E}+13$	0.0	3.60
54	$\text{C}_2\text{H}_6 + \text{CH}_3 = \text{C}_2\text{H}_5 + \text{CH}_4$	$5.50\text{E}+14$	0.0	21.50
55	$\text{C}_2\text{H}_6 + \text{O}_2 = \text{C}_2\text{H}_5 + \text{HO}_2$	$1.00\text{E}+13$	0.0	51.00
56	$\text{C}_2\text{H}_6 + \text{HO}_2 = \text{C}_2\text{H}_5 + \text{H}_2\text{O}_2$	$3.00\text{E}+11$	0.0	11.50
57	$\text{C}_2\text{H}_6 = \text{CH}_3 + \text{CH}_3 \text{ (pd)}$	$2.00\text{E}+32$	-5.0	92.23
58	$\text{C}_2\text{H}_5 = \text{C}_2\text{H}_4 + \text{H} \text{ (pd)}$	$7.00\text{E}+25$	-4.1	42.98
59	$\text{C}_2\text{H}_5 + \text{O}_2 = \text{C}_2\text{H}_4 + \text{HO}_2$	$1.50\text{E}+12$	0.0	4.86
60	$\text{C}_2\text{H}_5 + \text{CH}_3 = \text{C}_2\text{H}_4 + \text{CH}_4$	$7.90\text{E}+11$	0.0	0.0
61	$\text{C}_2\text{H}_4 + \text{M} = \text{C}_2\text{H}_2 + \text{H}_2 + \text{M}$	$3.00\text{E}+17$	0.0	79.28
62	$\text{C}_2\text{H}_4 + \text{M} = \text{C}_2\text{H}_3 + \text{H} + \text{M}$	$3.10\text{E}+17$	0.0	98.16
63	$\text{C}_2\text{H}_4 + \text{H} = \text{C}_2\text{H}_3 + \text{H}_2$	$1.50\text{E}+14$	0.0	10.20
64	$\text{C}_2\text{H}_4 + \text{O} = \text{CH}_3 + \text{HCO}$	$1.60\text{E}+09$	1.2	0.74
65	$\text{C}_2\text{H}_4 + \text{OH} = \text{C}_2\text{H}_3 + \text{H}_2\text{O}$	$1.00\text{E}+13$	0.0	0.0
66	$\text{C}_2\text{H}_4 + \text{CH}_3 = \text{CH}_4 + \text{C}_2\text{H}_3$	$4.20\text{E}+11$	0.0	11.20
67	$\text{C}_2\text{H}_4 + \text{O}_2 = \text{C}_2\text{H}_3 + \text{HO}_2$	$4.00\text{E}+13$	0.0	61.50
68	$\text{C}_2\text{H}_3 + \text{H} = \text{C}_2\text{H}_2 + \text{H}_2$	$1.00\text{E}+13$	0.0	0.0
69	$\text{C}_2\text{H}_3 = \text{C}_2\text{H}_2 + \text{H} \text{ (pd)}$	$6.60\text{E}+19$	-2.8	36.13
70	$\text{C}_2\text{H}_3 + \text{CH}_3 = \text{C}_2\text{H}_2 + \text{CH}_4$	$7.90\text{E}+11$	0.0	0.0
71	$\text{C}_2\text{H}_2 + \text{M} = \text{C}_2\text{H} + \text{H} + \text{M}$	$4.10\text{E}+16$	0.0	107.00
72	$\text{C}_2\text{H}_2 + \text{H} = \text{C}_2\text{H} + \text{H}_2$	$6.00\text{E}+13$	0.0	23.70
73	$\text{C}_2\text{H}_2 + \text{O} = \text{CH}_2 + \text{CO}$	$7.00\text{E}+03$	2.8	0.50
74	$\text{C}_2\text{H}_2 + \text{O} = \text{HCCO} + \text{H}$	$1.40\text{E}+04$	2.8	0.50

constants.

Other gas-phase reactions, including formation of PAHs, and their rate constants were given based on the kinetic models developed by Frenklach and Warnatz.⁽¹⁾

Table 1 (continued)

No.	Reaction	k = AT ⁿ exp(−E/RT)		
		A	n	E
		(cm ³ , mol, s)		(kcalmol ^{−1})
75	C2H2 + OH = CH2CO + H	1.00E+14	0.0	11.50
76	C2H2 + OH = C2H + H2O	2.70E+14	0.0	15.10
77	C2H + O2 = HCO + CO	2.40E+12	0.0	0.0
78	C2H + O2 = HCCO + O	6.00E+11	0.0	0.0
79	HCCO + H = CH2 + CO	1.50E+13	0.0	0.0
80	HCCO + O = HCO + CO	1.20E+12	0.0	0.0
81	I-C3H7 + M = C3H5 + H2 + M	1.00E+13	0.0	30.00
82	N-C3H7 + M = C3H6 + H + M	1.00E+14	0.0	37.28
83	I-C3H7 + M = C3H6 + H + M	2.00E+14	0.0	38.72
84	I-C3H7 + O2 = C3H6 + HO2	1.00E+12	0.0	5.00
85	N-C3H7 + O2 = C3H6 + HO2	1.00E+12	0.0	5.00
86	C3H6 + M = C2H3 + CH3 + M	1.00E+18	0.0	74.00
87	C3H6 + M = C3H5 + H + M	1.00E+13	0.0	78.00
88	C3H6 + H = C3H5 + H2	5.01E+13	0.0	3.50
89	C3H6 + OH = C3H5 + H2O	2.00E+13	0.0	3.06
90	C3H6 + O2 = C3H5 + HO2	1.00E+14	0.0	39.00
91	C3H5 + M = C3H4 + H + M	3.98E+13	0.0	70.00
92	C3H5 + CH3 + M = I-C4H8 + M	1.34E+13	0.0	0.0
93	C3H5 + O2 = C3H4 + HO2	6.00E+11	0.0	10.00
94	C3H5 + H = C3H4 + H2	1.00E+13	0.0	0.0
95	C3H5 + C2H4 = C3H6 + C2H3	3.20E+12	0.0	18.00
96	C3H4 + OH = CO + C2H5	5.00E+12	0.0	1.29
97	C3H4 + H = CH3 + C2H2	2.00E+13	0.0	2.41
98	C3H4 + OH = HCO + C2H4	1.00E+12	0.0	0.0
99	C3H4 + O = CO + C2H4	1.50E+13	0.0	2.10
100	C3H3 + H + M = C3H4 + M	2.00E+13	0.0	0.0
101	C3H3 + O = C3H2 + OH	3.20E+12	0.0	0.0
102	C3H3 + O2 = CH2CO + HCO	3.00E+10	0.0	2.87
103	C3H2 + H + M = C3H3 + M	6.00E+12	0.0	0.0
104	C3H2 + O = C2H + HCO	6.80E+13	0.0	0.0
105	C3H2 + OH = C2H2 + HCO	6.80E+13	0.0	0.0
106	C2H2 + CH2 = C3H3 + H	2.00E+12	0.0	0.0
107	I-C4H8 + OH = N-C3H7 + CH2O	1.50E+12	0.0	0.0
108	C2H5 + C2H3 + M = I-C4H8 + M	8.90E+12	0.0	0.0
109	C4H6 + OH = C2H5 + CH2CO	1.00E+12	0.0	0.0
110	C4H6 + OH = C3H5 + CH2O	1.00E+12	0.0	0.0
111	C4H6 + O = C2H4 + CH2CO	1.00E+12	0.0	0.0
112	C4H6 + O = C3H3 + CH2O + H	1.00E+12	0.0	0.0
113	C4H6 + H = C2H4 + C2H3	5.00E+11	0.0	0.0
114	C4H6 + C2H3 = C2H4 + 2C2H2	6.30E+13	0.0	14.50
115	C2H3 + C2H3 + M = C4H6 + M	8.90E+12	0.0	0.0
116	C4H6 + C2H3 = C2H4 + C4H4 + H	6.30E+13	0.0	14.50
117	C4H4 + H = N-C4H3 + H2	7.90E+13	0.0	14.50
118	C4H4 + C2H = C2H2 + N-C4H3	4.00E+13	0.0	0.0
119	C4H4 + C2H3 = C2H4 + N-C4H3	5.00E+11	0.0	16.30
120	C2H2 + C2H + M = N-C4H3 + M	3.90E+07	1.7	−1.60
121	C2H3 + C2H2 = C4H4 + H	1.60E+13	0.0	25.06
122	C4H4 + H = I-C4H3 + H2	3.10E+14	0.0	14.50
123	C4H4 + C2H = C2H2 + I-C4H3	4.00E+13	0.0	0.0
124	C4H4 + C2H3 = C2H4 + I-C4H3	5.00E+11	0.0	16.30
125	N-C4H3 + H = C4H2 + H2	1.00E+13	0.0	0.0
126	N-C4H3 + M = C4H2 + H + M	8.50E+15	0.0	60.00
127	C4H2 + M = C4H + H + M	3.50E+17	0.0	80.00
128	C4H2 + OH = C3H2 + HCO	6.69E+13	0.0	0.41
129	C4H2 + O = C3H2 + CO	7.86E+12	0.0	1.35
130	C4H + H2 = H + C4H2	4.00E+13	0.0	0.0
131	C2H2 + C2H = C4H2 + H	4.00E+13	0.0	0.0
132	I-C4H3 + H = C4H2 + H2	1.00E+13	0.0	0.0
133	A1 + M = A1− + H + M	5.00E+15	0.0	108.60
134	A1 + OH = A1− + H2O	2.10E+13	0.0	4.60
135	A1 + H = A1− + H2	2.50E+14	0.0	16.00
136	A1 + C2H = A1− + C2H2	5.00E+13	0.0	16.00
137	A1 + C2H3 = A1− + C2H4	5.00E+13	0.0	16.00
138	S-C6H5 = A1−	1.00E+10	0.0	0.0
139	N-C4H3 + C2H2 + M = A1− + M	7.00E+11	0.0	0.0
140	C1 + OH = CO + H	5.00E+13	0.0	0.0
141	C1 + O2 = CO + O	2.00E+13	0.0	0.0
142	C1 + CO2 = CO + CO	6.00E+08	0.0	0.0
143	C1 + CH3 = C2H2 + H	5.00E+13	0.0	0.0
144	C1 + CH2 = C2H + H	5.00E+13	0.0	0.0
145	CH + C2H2 + M = C3H3 + M	1.91E+13	0.0	0.0
146	CH + H = C1 + H2	1.51E+14	0.0	0.0
147	CH + O = CO + H	5.75E+13	0.0	0.0
148	CH + CH3 = C2H3 + H	3.00E+13	0.0	0.0

Table 1 (continued)

No.	Reaction	$k = A T^n \exp(-E/RT)$		
		A (cm ³ , mol, s)	n	E (kcalmol ⁻¹)
149	CH + C ₂ H ₂ = C ₃ H ₂ + H	1.30E+14	0.0	0.0
150	CH + OH = C ₁ + H ₂ O	3.00E+13	0.0	0.0
151	CH + O ₂ = CO + OH	1.35E+11	0.7	25.70
152	CH + O ₂ = HCO + O	1.00E+13	0.0	0.0
153	C ₂ H + OH = HCCO + H	2.00E+13	0.0	0.0
154	C ₂ H + O = CH + CO	5.00E+13	0.0	0.0
155	C ₂ H + C ₂ H ₃ = C ₂ H ₂ + C ₂ H ₂	3.00E+13	0.0	0.0
156	C ₂ H + C ₄ H ₂ = C ₆ H ₂ + H	4.00E+13	0.0	0.0
157	C ₂ H + C ₆ H ₂ = C ₈ H ₂ + H	1.00E+12	0.0	0.0
158	C ₂ H + M = C ₂ + H + M	4.67E+16	0.0	124.00
159	C ₂ H + H = C ₂ + H ₂	1.00E+12	0.0	0.0
160	C ₂ H + OH = C ₂ + H ₂ O	1.00E+12	0.0	0.0
161	C ₄ H + C ₂ H ₂ = C ₆ H ₂ + H	4.00E+13	0.0	0.0
162	C ₆ H + C ₂ H ₂ = C ₈ H ₂ + H	1.00E+12	0.0	0.0
163	C ₄ H ₂ + C ₄ H = C ₈ H ₂ + H	1.00E+12	0.0	0.0
164	C ₆ H ₂ + M = C ₆ H + H + M	5.00E+16	0.0	80.00
165	C ₂ H ₂ + O ₂ = HCO + HCO	1.00E+14	0.0	38.00
166	O ₂ + M = O + O + M	5.10E+15	0.0	115.00
167	H ₂ + O ₂ = OH + OH	1.70E+13	0.0	48.15
168	A ₁ - + C ₂ H = A ₁ C ₂ H	1.00E+14	0.0	0.0
169	A ₁ + C ₄ H = A ₁ - + C ₄ H ₂	2.00E+13	0.0	0.0
170	A ₁ C ₂ H + H = A ₁ - + C ₂ H ₂	1.00E+14	0.0	0.0
171	A ₁ C ₂ H + C ₂ H = A ₁ - + C ₄ H ₂	2.00E+13	0.0	0.0
172	A ₁ C ₂ H- + H = A ₁ C ₂ H	1.00E+13	0.0	0.0
173	A ₁ C ₂ H + H = A ₁ C ₂ H- + H ₂	1.00E+14	0.0	0.0
174	A ₁ C ₂ H + OH = A ₁ C ₂ H- + H ₂ O	2.10E+13	0.0	19.10
175	A ₁ C ₂ H + C ₂ H = A ₁ C ₂ H- + C ₂ H ₂	2.00E+13	0.0	0.0
176	A ₁ C ₂ H* + H = A ₁ C ₂ H	1.00E+13	0.0	0.0
177	A ₁ C ₂ H + H = A ₁ C ₂ H* + H ₂	1.00E+14	0.0	0.0
178	A ₁ C ₂ H + OH = A ₁ C ₂ H* + H ₂ O	2.10E+13	0.0	19.10
179	A ₁ C ₂ H + C ₂ H = A ₁ C ₂ H* + C ₂ H ₂	2.00E+13	0.0	0.0
180	A ₁ C ₂ H* + C ₂ H ₂ = A ₁ C ₂ HC ₂ H	1.00E+13	0.0	0.0
181	A ₁ C ₂ HC ₂ H = A ₂ -X	1.00E+10	0.0	0.0
182	A ₂ -X + H = A ₂	1.00E+13	0.0	0.0
183	A ₂ + H = A ₂ -X + H ₂	1.00E+14	0.0	0.0
184	A ₂ + OH = A ₂ -X + H ₂ O	2.10E+13	0.0	19.10
185	A ₂ + C ₂ H = A ₂ -X + C ₂ H ₂	2.00E+13	0.0	0.0
186	A ₂ -X + C ₂ H ₂ = A ₂ R ₅ + H	1.00E+13	0.0	0.0
187	A ₂ R ₅ - + H = A ₂ R ₅	1.00E+13	0.0	0.0
188	A ₂ R ₅ + H = A ₂ R ₅ - + H ₂	1.00E+14	0.0	0.0
189	A ₂ R ₅ + OH = A ₂ R ₅ - + H ₂ O	2.10E+13	0.0	19.10
190	A ₂ R ₅ + C ₂ H = A ₂ R ₅ - + C ₂ H ₂	2.00E+13	0.0	0.0
191	A ₂ R ₅ C ₂ H + H = A ₂ R ₅ - + C ₂ H ₂	1.00E+14	0.0	0.0
192	A ₂ R ₅ C ₂ H* + H = A ₂ R ₅ C ₂ H	1.00E+13	0.0	0.0
193	A ₂ R ₅ C ₂ H + H = A ₂ R ₅ C ₂ H* + H ₂	1.00E+14	0.0	0.0
194	A ₂ R ₅ C ₂ H + OH = A ₂ R ₅ C ₂ H* + H ₂ O	2.10E+13	0.0	19.10
195	A ₂ R ₅ C ₂ H + C ₂ H = A ₂ R ₅ C ₂ H* + C ₂ H ₂	2.00E+13	0.0	0.0
196	A ₂ R ₅ C ₂ H* + C ₂ H ₂ = A ₂ R ₅ C ₂ HC	1.00E+13	0.0	0.0
197	A ₂ R ₅ C ₂ HC = A ₃ R ₅ -	1.00E+10	0.0	0.0
198	A ₃ R ₅ - + H = A ₃ R ₅	1.00E+13	0.0	0.0
199	A ₃ R ₅ + H = A ₃ R ₅ - + H ₂	1.00E+14	0.0	0.0
200	A ₃ R ₅ + OH = A ₃ R ₅ - + H ₂ O	2.10E+13	0.0	19.10
201	A ₃ R ₅ + C ₂ H = A ₃ R ₅ - + C ₂ H ₂	2.00E+13	0.0	0.0
202	A ₃ R ₅ - + C ₂ H ₂ = A ₃ R ₅ C ₂ H ₂	1.00E+13	0.0	0.0
203	A ₃ R ₅ C ₂ H ₂ = A ₄ R ₅ + H	1.00E+10	0.0	0.0
204	A ₄ R ₅ - + H = A ₄ R ₅	1.00E+13	0.0	0.0
205	A ₄ R ₅ + H = A ₄ R ₅ - + H ₂	1.00E+14	0.0	0.0
206	A ₄ R ₅ + OH = A ₄ R ₅ - + H ₂ O	2.10E+13	0.0	19.10
207	A ₄ R ₅ + C ₂ H = A ₄ R ₅ - + C ₂ H ₂	2.00E+13	0.0	0.0
208	A ₄ R ₅ C ₂ H + H = A ₄ R ₅ - + C ₂ H ₂	1.00E+14	0.0	0.0
209	A ₄ R ₅ C ₂ H* + H = A ₄ R ₅ C ₂ H	1.00E+13	0.0	0.0
210	A ₄ R ₅ C ₂ H + H = A ₄ R ₅ C ₂ H* + H ₂	1.00E+14	0.0	0.0
211	A ₄ R ₅ C ₂ H + OH = A ₄ R ₅ C ₂ H* + H ₂ O	2.10E+13	0.0	19.10
212	A ₄ R ₅ C ₂ H + C ₂ H = A ₄ R ₅ C ₂ H* + C ₂ H ₂	2.00E+13	0.0	0.0
213	A ₄ R ₅ C ₂ H* + C ₂ H ₂ = A ₅ R ₅ -	1.00E+13	0.0	0.0
214	A ₅ R ₅ - + H = A ₅ R ₅	1.00E+13	0.0	0.0
215	A ₅ R ₅ + H = A ₅ R ₅ - + H ₂	1.00E+14	0.0	0.0
216	A ₅ R ₅ + OH = A ₅ R ₅ - + H ₂ O	2.10E+13	0.0	19.10
217	A ₅ R ₅ + C ₂ H = A ₅ R ₅ - + C ₂ H ₂	2.00E+13	0.0	0.0
218	A ₅ R ₅ - + C ₂ H ₂ = A ₆ R ₅ + H	1.00E+13	0.0	0.0

(pd) Pressure-dependent rate constant, fit at 1 atm.

Since primary soot particles emitted from practical combustors are said to have as many as $10^6 - 10^{12}$ carbon atoms, the following treatments were introduced to facilitate calculation. First, so as to include clusters with large cluster numbers, clusters

Fig. 1 Mass fractions of soot and some gaseous species in ethylene-air mixture pyrolysis calculated by omitting reaction (3)

bigger than 50-mer were lumped into finite groups, each group consisting of a certain range of classes. The kinetic equation for each group was easily derived by taking the summation of the $d[C_n]/dt$ after weighting by n . Since the factors determining the size of the primary soot particles were unknown, the upper limit of class n^* was assumed. At this limit, the boundary condition that $\partial^2 C/\partial n^2 = 0$ was imposed, and it was assumed that the cluster flux across n^* was quasi-steady. As has been reported already⁽⁵⁾, there is a limit of n^* beyond which the total soot yield on a mass basis is no longer affected. The computational method was basically a step-by-step numerical integration of ordinary simultaneous differential equations, in a fully implicit manner, in terms of time and cluster class.

3. Results

First, we made full kinetic calculations omitting the cluster reactions of the polyacetylene radical C₂H, reaction (3), to observe the significance of C₂H during soot formation. Figure 1 shows the calculated mass fraction versus time relations for soot and some gaseous species in ethylene-air mixture pyrolysis at $T=800$ K. The concentrations of most species agree fairly well with the calculated results based on a rate-controlled partial equilibrium, shown in Fig. 3 of Ref. (5). However, carbon vapors C₃ - C₅, the major colliding partners for the cluster growth mechanism, are scarcely formed in the case of the present kinetic calculation and production of soot clusters no longer takes place. This indicates that clustering reactions other than those through carbon vapors must be essential. For this reason, we took into account the cluster reaction between C_n and C₂H in further calculations.

Figure 2 shows the calculated mass ratio of soot to carbon in the fuel for the case of pyrolysis of 1.09%

C_2H_2 in Ar under a shock-heated condition, with conditions being the same as those of the shock-tube experiment performed by Frenklach et al.⁽³⁾ The soot mass defined here was the total mass of the clusters having classes greater than five. The cluster classes that should be classified as soot are rather ambiguous, but the lower classes do not affect the total soot mass since the mass of carbon contained within soot clusters was concentrated upon high n -mers. As can be

Fig. 2 Conversion ratio of carbon in fuel to soot for C_2H_2 -Ar mixture under a shock-heated condition

Fig. 3 Mass fractions of soot and some gaseous species in shock-heated pyrolysis of C_2H_2 -Ar mixture at $T = 2100$ K

Fig. 4 Mass fractions of soot and some gaseous species in shock-heated pyrolysis of C_2H_2 -Ar mixture at $T = 2300$ K

seen from the figure, the well known bell-shaped temperature dependence of the soot yield having a peak at around 2000 K is reproduced well by the proposed theory. However, the predicted conversion ratio from fuel to soot shows a value two times higher than that of the experiments. Details will be discussed in the next section.

In Figs. 3 and 4, the calculated mass fraction versus time relations for soot clusters, C, C_2 , C_3 , C_2H and some gaseous species in shock-heated acetylene pyrolysis under $p = 0.5$ MPa at $T = 2100$ K and $T = 2300$ K are shown, respectively. At $T = 2100$ K, C_2H reaches a high concentration in earlier stages of the pyrolysis and then increases gradually as time goes on. On the other hand, carbon vapors sharply increase with time preceding the soot formation and subsequently decrease. Such profiles suggest that the formation of small clusters significantly depend on the reaction with C_2H , while the formation of large clusters depend on reaction with carbon vapors. At $T = 2300$ K, which has a much shorter induction period, final mass fraction of soot is much lower than that at $T = 2100$ K. This is because the equilibrium of cluster reactions shifts towards declustering at higher temperatures thereby reducing final value of the mass fraction of soot. This will be also discussed in the next section.

Figure 5 shows the pressure effect on soot yield, showing the well-known fact that the increase in pressure increases soot yield. This is consistent with a simple equilibrium consideration in that the condensed phase should become stable with pressure. Furthermore, the results also show that the pressure affects the induction period for soot formation.

4. Discussion

To elucidate the mechanism of clustering in detail, a sensitivity analysis was performed. The sensitivity coefficients are⁽⁹⁾

Fig. 5 Pressure dependence of soot yield in shock-heated pyrolysis of C_2H_2 -Ar mixture

$$\beta_{nk} = \frac{A_k}{Y_{\max}} \frac{\partial Y_n}{\partial A_k}(t) \quad (8)$$

where β_{nk} is the sensitivity coefficient for change in the mass fraction of the n -mer due to a small change in the temperature-independent factor of the k -th reaction rate constant, A_k . $Y_{\max}$ is the maximum value of Y_n , mass fraction of n -mer, that is given in the calculation.

Figures 6 and 7 show the sensitivity coefficients of C_{100} and C_{10^5} , respectively, for the cluster reactions (1) and (3) at $T=2100$ K. As can be seen from the figures, the reaction with C_2H is the most significant rate-limiting step for formation and/or growth of small clusters like C_{100} , while the production of large clusters such as 10^5 -mer greatly depends on the reactions with carbon vapors. The sensitivity analysis for the supply of C_2H led to the following results: the initiation step for C_2H production is reaction (71) in Table 1. Once C_2H is accumulated, cluster reaction (3) boosts H atom production, which promotes the continued formation of C_2H in a chain like manner by reaction (72) and reverse reaction of reaction (131) in

Fig. 6 Sensitivity coefficient of C_{100} for cluster reactions in shock-heated pyrolysis of C_2H_2 -Ar mixture at $T=2100$ K

Fig. 7 Sensitivity coefficient of C_{10^5} for cluster reactions in shock-heated pyrolysis of C_2H_2 -Ar mixture at $T=2100$ K

Table 1. This chain like mechanism may be responsible for an extremely fast nucleation or formation of small clusters.

Figure 8 shows the sensitivity coefficients of C_{100} for the cluster reactions (1) and (3) at a higher temperature of $T=2300$ K. It should be noted that the sensitivities for carbon vapors are negative. This shows that at such a high temperature the reverse reaction of reaction (1) is much faster than the forward reaction. For this reason, soot formation no longer proceeds quickly, and this results in the bell-shaped temperature dependence as shown in Fig. 2.

Now, we shall discuss the reason why the calculated soot yield is almost two times greater than the experimental one as shown in Fig. 2. Although detailed chemical kinetics were taken into consideration in the calculation, reactions between C_3 and gaseous species except cluster reactions (1) and (3) were excluded because of the lack of available kinetic data. Under such circumstances of limited pathways, C_3 , having a higher Gibbs free energy, is hardly decomposed to other gaseous species and remains at a higher concentration. This prevents the declustering process in which C_3 is produced (reverse reactions of reactions (1) and (3)) since higher C_3 concentration leads to overestimation of the forward reaction of reaction (1) in the calculation. Figure 4 supports this explanation, showing much higher C_3 concentration in the range of soot formation. In summary, the lack of detailed C_3 kinetics data overestimates the forward reaction rate of the clustering at the higher temperature of 2300 K, and this results in higher soot yields in comparison with experiments. It is noted that further clarification is required for this.

Figure 9 shows the temperature dependence of PAH concentration under the same conditions. PAHs also shows bell-shaped temperature dependence, but the temperature range largely differs from those of

Fig. 8 Sensitivity coefficient of C_{100} for cluster reactions in shock-heated pyrolysis of C_2H_2 -Ar mixture at $T=2300$ K

Fig. 9 Temperature dependence of PAH formation in shock-heated pyrolysis of C_2H_2 -Ar mixture at $T = 2100$ K

Fig. 10 Effect of seed nuclei on soot production in shock-heated pyrolysis of C_2H_2 -Ar mixture at $T = 2100$ K

experiments. This suggests that in the case of shock heating to a very high temperature, soot is not formed merely through the production of PAHs. This is not meant to deny, however, the well-known role played by PAHs as the trigger of condensation and polymerization reactions in the subsequent step of soot formation in laminar flames in which PAHs might be formed in the low-temperature upstream region. To clarify if PAHs formed upstream of the maximum temperature can play a role as nuclei in subsequent stages, the calculation was carried out in which nuclei formed by heterogeneous condensation were simulated assuming the initial cluster concentrations of 6-mer and 12-mer to be 10^{-8} and 10^{-6} in mole fraction, respectively, instead of assuming existing temperature history. In Fig. 10 the results of the calculation at $T = 2100$ K are presented. It is shown that such seed nuclei affect not only the final soot yield but also the induction period for sooting. This suggests that the

derivatives formed as a result of the dehydrogenation of a PAH may behave like young clusters, thereby promoting soot growth. This also requires detailed clarification.

5. Conclusions

This theory, with detailed chemical kinetics based on the cluster mechanism, successfully elucidates rapid soot formation at higher temperatures. The results suggest the likelihood of soot formation via carbon clusters. It is also suggested that carbon vapors and C_2H are likely condensable species in the clustering process. It is shown that the small clusters are mainly generated via C_2H and grow into large clusters by reaction with carbon vapors at moderately high temperatures, whereas they are decomposed into carbon vapors at very high temperatures. Furthermore, the effects of pressure and heterogeneous nuclei on soot formation are discussed.

Acknowledgments

This study was supported by a Grant-in-Aid for Research on Priority Areas "Exploration of Combustion Mechanism," (No. 01627006) appropriated by the Ministry of Education, Science and Culture of Japan. Computations were carried out on FACOM M 780 and HITAC M 680 computers at the Data Processing Centers of Kyoto University and Ritsumeikan University, respectively.

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