

Supporting information

Thermal decomposition and oxidation of CH₃OH

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Table S-1. The reaction mechanism of the pyrolysis and oxidation of CH₃OH

Reaction	A*	n*	Θ*	Reference
1. CH ₃ OH+M=products	6.23E-07	0	38784	this study
1a. CH ₃ OH+M= ¹ CH ₂ +H ₂ O+M	1.25E-07	0	38784	this study
1b. CH ₃ OH+M=CH ₃ +OH+M	4.72E-07	0	38724	this study
1c. CH ₃ OH+M=CH ₂ OH+H+M	6.08E-07	0	46064	13
2. ¹ CH ₂ +M= ³ CH ₂ +M	1.50E-11	0	302	16
3. ³ CH ₂ +O ₂ →products	2.74E-11	0	874	19
3a-1. ³ CH ₂ +O ₂ →OH+H+CO	5.48E-12	0	874	19
3a-2. ³ CH ₂ +O ₂ →2H+CO ₂	5.48E-12	0	874	19
3b. ³ CH ₂ +O ₂ →O+CH ₂ O	2.19E-12	0	874	19
3c-1. ³ CH ₂ +O ₂ →H ₂ O+CO	7.13E-12	0	874	19
3c-2. ³ CH ₂ +O ₂ →H ₂ +CO ₂	7.13E-12	0	874	19
4. ¹ CH ₂ +O ₂ =products				
4b. ¹ CH ₂ +O ₂ =O+CH ₂ O	4.65E-11	0	0	this study
5. H+O ₂ =OH+O	1.38E-10	0	7253	21
6. CH ₃ +O ₂ =products				
6a. CH ₃ +O ₂ =CH ₃ O+O	5.91E-11	0	15347	16
6b. CH ₃ +O ₂ =CH ₂ O+OH	3.48E-12	0	10299	16
7. OH+H ₂ =H+H ₂ O	3.55E-16	1.5	17377	11
8. ³ CH ₂ +H ₂ =CH ₃ +H	8.31E-19	2.0	3640	13
9. ¹ CH ₂ +H ₂ =CH ₃ +H	1.16E-10	0	0	23
10. CH ₃ +H ₂ =CH ₄ +H	9.12E-21	2.7	4740	13
11. OH+CH ₃ OH=CH ₂ OH+H ₂ O	2.96E-16	1.4	57	11
12. OH+CH ₃ OH=CH ₃ O+H ₂ O	1.50E-22	3	-97.3	11
13. CH ₃ +CH ₃ OH=CH ₂ OH+CH ₄	2.59E-12	0	2887	11
14. CH ₃ +CH ₃ OH=CH ₃ O+CH ₄	1.66E-17	1.5	5005	16
15. H+CH ₃ OH=CH ₂ OH+H ₂	6.61E-11	0	3067	11
16. H+CH ₃ OH=CH ₃ O+H ₂	6.98E-18	2.1	2452	16
17. ³ CH ₂ +CH ₃ OH=CH ₃ O+CH ₃	9.58E-23	3.04	32.7	26 ***
18. ¹ CH ₂ +CH ₃ OH=CH ₃ +CH ₂ OH	6.64E-11	0	-277	16
19. O+CH ₃ OH=OH+CH ₂ OH	6.45E-19	2.5	1561	16
20. O+CH ₃ OH=OH+CH ₃ O	2.16E-19	2.5	2517.6	16
21. CH ₂ OH+M=CH ₂ O+H+M	7.48E+01	-2.5	17200	13
22. CH ₃ O+M=CH ₂ O+H+M	8.97E-11	0	6790.9	13
23. CH ₂ O+M=HCO+H+M	1.02E-08	0	38725	11
24. CH ₂ O+M=H ₂ +CO+M	4.67E-09	0	32110	11
25. HCO+M=H+CO+M	6.00E-11	0	7726	11
26. OH+OH=O+H ₂ O	7.19E-21	2.7	-917.4	11
27. CH ₃ +OH= ¹ CH ₂ +H ₂ O	1.15E-09	-0.48	0	11
28. CH ₃ +OH=CH ₂ O+H ₂	3.39E-14	0.6	-892	13
29. ³ CH ₂ +OH=CH ₂ O+H	1.11E-10	0	9.1	11
30. CH ₃ +CH ₃ (+M)=C ₂ H ₆ (+M)**	1.12E-07	-1.2	329	11
31. CH ₃ +CH ₃ =C ₂ H ₅ +H	5.27E-11	0	7392	11
32. CH ₃ + ³ CH ₂ =C ₂ H ₄ +H	1.89E-10	-0.1	8.2	11

33. $^3\text{CH}_2+^3\text{CH}_2=\text{C}_2\text{H}_3+\text{H}$	2.39E-10	0	17.1	11
34. $^3\text{CH}_2+^3\text{CH}_2=\text{C}_2\text{H}_2+\text{H}_2$	1.66E-11	0	0	11
35. $\text{O}+\text{H}_2=\text{OH}+\text{H}$	8.44E-20	2.7	3168.6	11
36. $\text{O}+^3\text{CH}_2=\text{H}+\text{HCO}$	1.33E-10	0	0	16
37. $\text{O}+^1\text{CH}_2=\text{H}_2+\text{CO}$	2.49E-11	0	0	16
38. $\text{O}+^1\text{CH}_2=\text{H}+\text{HCO}$	2.49E-11	0	0	16
39. $\text{O}+\text{CH}_3=\text{CH}_2\text{O}+\text{H}$	1.15E-10	0	0	13
40. $\text{O}+\text{CH}_3=\text{H}_2+\text{CO}+\text{H}$	2.52E-11	0	0	11
41. $\text{C}_2\text{H}_5+\text{M}\rightarrow\text{C}_2\text{H}_4+\text{H}+\text{M}$	1.66E-07	0	15609	16
42. $\text{C}_2\text{H}_3+\text{M}\rightarrow\text{C}_2\text{H}_2+\text{H}+\text{M}$	4.98E-09	0	16113	16
43. $\text{CH}_2\text{O}+\text{OH}=\text{H}_2\text{O}+\text{HCO}$	5.70E-15	1.2	-225	11
44. $\text{CH}_2\text{O}+\text{CH}_3=\text{CH}_4+\text{HCO}$	1.66E-11	0	3067	11
45. $\text{CH}_2\text{O}+\text{H}=\text{H}_2+\text{HCO}$	4.17E-11	0	2012	11
46. $\text{CH}_2\text{O}+\text{O}=\text{OH}+\text{HCO}$	6.93E-13	0.6	1390	11
47. $\text{CH}_2\text{O}+^3\text{CH}_2=\text{CH}_3+\text{HCO}$	1.23E-25	4.2	817	16
48. $\text{CH}_2\text{O}+^1\text{CH}_2=\text{CH}_3+\text{HCO}$	6.64E-11	0	-277	16
49. $\text{CH}_2\text{OH}+\text{HCO}=2\text{CH}_2\text{O}$	2.49E-11	0	0	16
50. $\text{OH}+\text{C}_2\text{H}_6=\text{H}_2\text{O}+\text{C}_2\text{H}_5$	5.88E-18	2.1	438	16
51. $\text{CH}_3+\text{C}_2\text{H}_6=\text{CH}_4+\text{C}_2\text{H}_5$	1.02E-17	1.7	5262	16
52. $\text{H}+\text{C}_2\text{H}_6=\text{H}_2+\text{C}_2\text{H}_5$	1.91E-16	1.9	3792	11
53. $\text{O}+\text{C}_2\text{H}_6=\text{OH}+\text{C}_2\text{H}_5$	1.88E-10	0	3950	11
54. $\text{OH}+\text{C}_2\text{H}_4=\text{H}_2\text{O}+\text{C}_2\text{H}_3$	3.36E-11	0	2990	16
55. $\text{CH}_3+\text{C}_2\text{H}_4=\text{CH}_4+\text{C}_2\text{H}_3$	3.77E-19	2	4632	16
56. $\text{H}+\text{C}_2\text{H}_4=\text{H}_2+\text{C}_2\text{H}_3$	2.19E-18	2.5	6163	16
57. $\text{O}+\text{C}_2\text{H}_4=\text{H}+\text{CH}_2\text{CHO}$	1.11E-17	1.8	111	16
58. $^1\text{CH}_2+\text{C}_2\text{H}_4=\text{CH}_3+\text{C}_2\text{H}_3$	6.64E-11	0	-277	16
59. $^3\text{CH}_2+\text{C}_2\text{H}_4=\text{CH}_3+\text{C}_2\text{H}_3$	2.66E-12	0	2661	16
60. $^3\text{CH}_2+\text{C}_2\text{H}_4\rightarrow\text{aC}_3\text{H}_5+\text{H}$	2.66E-12	0	2661	16
61. $\text{aC}_3\text{H}_5+\text{M}\rightarrow\text{C}_3\text{H}_4+\text{H}+\text{M}$	1.83E-09	0	19688	16
62. $\text{H}+\text{C}_2\text{H}_3(+\text{M})=\text{C}_2\text{H}_4(+\text{M})^{**}$	1.01E-11	0.3	141	16
63. $\text{HO}_2+\text{M}=\text{H}+\text{O}_2+\text{M}$	7.61E-10	0	22531	11
64. $\text{HO}_2+\text{CH}_2\text{O}=\text{HCO}+\text{H}_2\text{O}_2$	1.66E-12	0	0	16
65. $\text{HO}_2+\text{OH}=\text{H}_2\text{O}+\text{O}_2$	2.34E-10	-0.2	-56	11
66. $\text{HO}_2+\text{CH}_3=\text{CH}_4+\text{O}_2$	1.66E-12	0	0	16
67. $\text{HO}_2+\text{CH}_3=\text{CH}_3\text{O}+\text{OH}$	6.28E-11	0	0	16
68. $\text{H}+\text{HO}_2=\text{H}_2+\text{O}_2$	7.44E-11	0	538	16
69. $\text{H}+\text{HO}_2=\text{O}+\text{H}_2\text{O}$	6.59E-12	0	338	16
70. $\text{H}+\text{HO}_2=2\text{OH}$	1.40E-10	0	320	16
71. $\text{O}+\text{HO}_2=\text{OH}+\text{O}_2$	3.32E-11	0	0	16
72. $^3\text{CH}_2+\text{HO}_2=\text{CH}_2\text{O}+\text{OH}$	3.32E-11	0	0	16
73. $\text{OH}+\text{C}_2\text{H}_2=\text{H}+\text{CH}_2\text{CO}$	3.62E-28	4.5	-503.5	16
74. $\text{OH}+\text{CO}=\text{CO}_2+\text{H}$	7.91E-17	1.2	35.2	16
75. $\text{HO}_2+\text{CO}=\text{OH}+\text{CO}_2$	2.49E-10	0	11883	16
76. $\text{H}+\text{CH}_3(+\text{M})=\text{CH}_4(+\text{M})^{**}$	2.31E-08	-0.5	270	16
77. $\text{H}+\text{HCO}=\text{H}_2+\text{CO}$	1.22E-10	0	0	16
78. $\text{CH}+\text{H}_2=\text{H}+^3\text{CH}_2$	1.79E-10	0	1566	16

Reverse reaction is considered when connected by “ = “.

* $k = A T^n \exp(-\Theta/T)$, in the units of molecule, cm^3 , s, K.

** Parameters in the high pressure limit are shown; the rate is evaluated in the fall-off region by using the Troe's formula with the parameters given in Ref. 16.

*** The modified Arrhenius parameters are estimated by the non-linear least squares fit to the calculation given in Ref. 26 for $T = 1000 - 3000$ K.