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Selective Methane Oxidation Over Promoted Oxide Catalysts

Quarterly Report
June - August 1995

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Work Performed Under Contract No.: DE-FG21-92MC29228

For
U.S. Department of Energy
Office of Fossil Energy
Morgantown Energy Technology Center
Morgantown, West Virginia

By
Lehigh University
Department of Chemistry
Bethlehem, Pennsylvania 18015

Disclaimer

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SELECTIVE METHANE OXIDATION OVER PROMOTED OXIDE CATALYSTS

SUMMARY OF PROGRESS

During this quarter, a kinetics model that includes both gas phase and surface reactions was developed in order to study the process of methane partial oxidation to oxygenates. The model was used to investigate a variety of problems, such as the importance of the first-bed catalyst in the double-bed reactor configuration, the role of gas phase and surface reactions in the partial oxidation reaction, and the effect of pressure. New V_2O_5/SiO_2 catalysts were prepared as xerogels and were utilized, with different V_2O_5 contents, as both of the beds in the double bed reactor configuration, and these experiments will be described in the next quarterly progress report when data analysis is completed.

Calculations from the model showed that under the reaction conditions employed previously in this work for the partial oxidation of methane to methanol and formaldehyde in the double-bed reactor, a certain percentage of methyl radicals generated by the first catalyst bed *can* survive long enough to reach the second bed. At 600°C with a methane/air ratio of 1.5, as much as 5.7% of the methyl radicals generated by the first catalyst layer will reach the second catalyst layer to undergo further reactions. The methyl radical concentration decreased exponentially with distance from origin, making it a necessity to position the two layers of catalysts as close as possible. However, the model predicts that a significantly higher percentage of methyl radicals will arrive at the second layer at lower pressure.

The relative importance of gas phase and surface reactions in oxygenate formation was also investigated with the model. Under the experimental conditions studied, it appears that a large percentage of the formaldehyde is formed in the gas phase. The further oxidation of formaldehyde, however, is mostly a surface reaction because the model predicts that a large amount of formaldehyde would accumulate without the presence of a catalytic surface. According to the model, formation and reaction of methanol mainly occurs on the surface rather than in the gas phase since the gas phase reactions involving methanol are negligible as far as oxygenate production is concerned. Taking reactions involving methanol reactions out of the model has negligible effect on the formaldehyde reactions.

An advantage of any modeling work is that once a reasonable model is established it can be used to predict results that would be otherwise difficult to obtain experimentally. Although experiments were routinely carried out under atmospheric pressure in this project, it is instructive to extrapolate the experimental data to higher pressures using the model. In this way, insights may be gained as to how the relative importance of surface and gas phase reactions changes when the reaction pressure would be increased. Using the gas phase model, the modeling results indicated that increasing pressure would cause increases in both methane conversion and oxygenate selectivities, mainly because of the increased importance of gas phase free radical reactions as opposed to reactions on the catalyst surface. The increased yield of oxygenates is probably due to a faster rate of oxygenate formation due to higher pressure than the rate of oxygenate decomposition, which is mainly a surface process.

SELECTIVE METHANE OXIDATION OVER PROMOTED OXIDE CATALYSTS

OBJECTIVES OF THE RESEARCH

The objective of this research project is the selective oxidative coupling of methane to C_2 hydrocarbons (Equations 1-3) and oxygenates, in particular formaldehyde and methanol as represented by Equations 4 and 5. Air, oxygen, or carbon dioxide, rather than nitrous oxide will be utilized as the oxidizing gas at high gas hourly space velocity, but mild reaction conditions (500-700°C and 0.1 MPa total pressure). All the investigated processes are catalytic, aiming at minimizing gas phase reactions that are difficult to control.

$$2CH_4 + \tfrac{1}{2}O_2 \rightleftharpoons C_2H_6 + H_2O \tag{1}$$
$$2CH_4 + O_2 \rightleftharpoons C_2H_4 + 2H_2O \tag{2}$$
$$2CH_4 + 2CO_2 \rightleftharpoons C_2H_4 + 2CO + 2H_2O \tag{3}$$
$$CH_4 + O_2 \rightleftharpoons CH_2O + H_2O \tag{4}$$
$$CH_4 + \tfrac{1}{2}O_2 \rightleftharpoons CH_3OH \tag{5}$$

Initially chosen for this research were oxide catalysts have been that are surface doped with small amount of acidic dopants. It was proposed that the very basic SrO/La_2O_3 catalyst, which is active in the formation of methyl radicals, could be doped with acidic oxides or other groups to increase further its activity in forming methyl radicals that could be utilized to increase the productivity of C_2 products or be converted to oxygenates.

The research to be carried out under this U.S. DOE-METC contract is divided into the following three tasks:

Task 1. Maximizing Selective Methane Oxidation to C_2 Products Over Promoted Sr/La_2O_3 Catalysts.
Task 2. Selective Methane Oxidation to Oxygenates.
Task 3. Catalyst Characterization and Optimization.

Task 1 dealt with the preparation, testing, and optimization of acidic promoted lanthana-based catalysts for the synthesis of C_2 hydrocarbons and is completed. Task 2 aims at the formation and optimization of promoted catalysts for the synthesis of oxygenates, in particular formaldehyde and methanol. Task 3 involves characterization of the most promising catalysts so that optimization can be achieved under both Task 1 and Task 2.

SELECTIVE METHANE OXIDATION OVER PROMOTED OXIDE CATALYSTS

RESEARCH PROGRESS

Introduction

The partial oxidation of methane to oxygenates involves a complex network of heterogeneous and homogeneous free radical reactions, particularly under higher temperatures and pressures. It is generally difficult to separately study the relative importance of each of these types of reactions during the reaction process by experimental means. However, in order to maximize the oxygenate yields, better reactor/reaction designs, such as the double-bed reactor configuration explored previously in this project, are needed. For these tasks, it is often necessary to understand the extent to which each of these two different types of reactions contributes to the reaction process. Therefore, during this quarter, efforts were made in this aspect through a kinetic modeling approach. With such an approach, one can readily examine the contribution of each and every reaction step in the reaction process, simply by including or excluding it from the model.

A kinetic model consisting of both gas phase free radical reactions and certain surface reaction steps was assembled. In the gas phase part of the model, most elementary reaction steps involving radicals, such as CH_3, OH, O, H, HO_2, CH_3, etc., were included. In the heterogenous part of the model, only the most important surface steps of interest were considered. The rate constant data for the gas phase reactions were obtained from a gas phase kinetics database released by the National Institute of Standard and Technology (1), while those for the surface reactions were obtained empirically by utilizing experimental data. The computer program used for the kinetics calculations was developed by the National Institute of Standard and Technology and is known as ACUHEM (2). This program is compiled for the PC platform with machines with math coprocessors and can solve up to 200 simultaneous differential equations, which is necessary when there are many possible intermediate species and is commonly seen in gas phase chemical kinetics. Despite the relatively unfriendly user interface, the program provides a time profile of the concentrations of all the species at a resolution of 0.001 sec within less than a minute.

Results

The Double-Layered Catalyst Bed

The double-layered catalyst bed can be modeled by including a methyl radical generating step in the model to simulate the chemistry of the first catalyst layer, i.e.

$$CH_4 \underset{layer}{\overset{1st}{\Rightarrow}} \bullet CH_3.$$

In order not to disturb the gas phase reactions with unnecessary gas phase free radicals such as H, the above step was not balanced in the model. An experiment was carried out at 600°C with a methane-to-air ratio of 1.5 over the first catalyst layer that was utilized previously, i.e. 1 wt% $SO_4^{2-}/SrO/La_2O_3$ (see Report DOE/MC/29228-10). The rate of methane consumption was measured by product analysis, and the rate constant for the above reaction step was calculated to be $k = 1.324\ sec^{-1}$. A series of calculations was then carried out at 600°C with a methane-to air ratio of 1.5 in which the concentrations of the reactants, intermediates, and products were obtained as a function of residence time. This provided for the calculation of the quantity of methyl radicals produced and consumed in the first catalyst layer. The percentages of methyl radicals that could exit the first layer at various residence time, defined as P, and enter a second catalyst bed are shown in the last column of Table 1.

Table 1. Calculated results of methane conversions, product selectivities, and the percentages of methyl radicals that could exit the first layer at various residence time for initial CH_4/Air = 1.5 at 600°C and 0.1 MPa.

Residence Time (sec)	CH_4 Conv. (mol%)	Product Selectivities (mol%)						P (%)
		C_2H_4	C_2H_6	CO_2	CO	CH_2O	CH_3OH	
0.001	0.097	0.0	92.2	0.0	0.0	2.0	0.0	5.636
0.002	0.270	0.1	95.6	0.0	0.0	2.1	0.0	2.026
0.005	0.674	0.3	96.5	0.0	0.1	2.2	0.0	0.810
0.008	1.078	0.6	96.5	0.0	0.2	2.3	0.0	0.505
0.010	1.346	0.7	96.4	0.0	0.2	2.3	0.0	0.404
0.100	13.21	10.6	77.9	0.0	6.4	5.0	0.0	0.036
0.200	25.57	18.7	52.9	0.4	23.3	4.6	0.0	0.016
0.300	35.94	17.4	50.0	0.8	30.7	1.0	0.0	0.012
0.400	43.66	19.1	53.1	0.7	26.8	0.2	0.0	0.009
0.500	50.00	21.4	54.2	0.6	23.7	0.0	0.0	0.007

It is evident from this table that at short residence time (high gas hourly space velocity) and low methane conversion, as much as 5.7% of the methyl radicals generated by the first catalyst layer can reach the second bed for further reaction. Although this quantity (P) decreased exponentially as a function of residence time (or the distance along the reactor axis), a non-zero value was maintained throughout the range of experimental interest. Therefore, under most reaction conditions, the first catalyst layer can always provide a certain quantity of methyl radicals to the second layer. In actual experiments in which the double-layered catalyst bed was employed, the two catalyst layers were physically packed one on top of the other. The two layers of catalysts are not only in contact with each other, but to a degree there was an actual overlap of the two catalysts near the interface on a microscopic scale. Therefore, it is often difficult to calculate an accurate residence time for a particular reactor configuration. In the vicinity of the interface, a much larger percentage of methyl radicals will arrive at the second layer due to the much shorter distance between the two layers. As a result, the oxygenate formation could be higher than expected.

In addition to the calculated results at 0.1 MPa shown in Table 1, the computations were also carried out at lower and higher pressures, and the results are depicted in Figure 1. Evidently a significantly higher percentage of methyl radicals will arrive at the second layer when the total pressure of the reagent mixture is reduced. Thus, lower pressures are beneficial to higher oxygenate yield under a double-bed configuration.

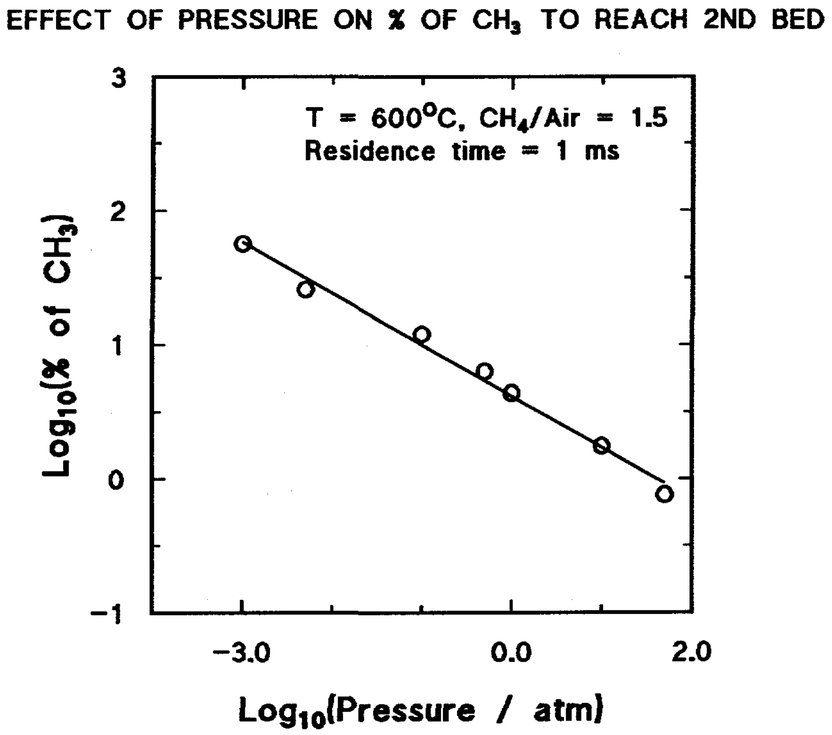

Figure 1. The quantity of methyl radicals that survive to reach the second catalyst layer as a function of the log of the reaction pressure. Computations are for CH_4/Air = 1.5 at 600°C and with a residence time of 1 millisec.

It is also evident from Table 1 that as the residence time increased, the formaldehyde selectivity increased and reached a maximum at a residence time of about 0.1 sec. Since in these calculations the only surface reaction was the methyl radical generation step, this maximum reflects an increased gas phase rate of formaldehyde removal at longer residence times as compared to the formaldehyde formation rate. The significance of this result is that this information can be used to adjust the reaction conditions in order to obtain the maximum yield of oxygenates. Considering the relatively high methane conversions, the formaldehyde selectivity near the maximum is very significant. Since there were no surface reaction steps included in the model to remove formaldehyde, this accumulation of formaldehyde is most likely to be due to gas phase reactions.

It is noted that according to these calculations (Table 1), methanol was not a gas phase product even with an additional source of methyl radicals from the surface. The experimentally observed methanol production with a double-layered catalyst bed consisting of 1 wt% $SO_4^{2-}/SrO/La_2O_3||$1 wt% V_2O_5/SiO_2 (see Report DOE/MC/29228-10) must be due to a process that involves surface reactions.

Consistent with experimental results, Table 1 also shows that the model predicts a high selectivity of coupling products under these conditions, indicating that the coupling reaction to form ethane is favored at shorter residence time. The higher selectivities of C_2 obtained from the model, as compared with those obtained from experiments, are a result of a lack of surface reactions that lead to transformation of the methyl radicals to other products.

The Gas-Phase Model

The entire list of gas phase elementary reaction steps on which the double-layered-catalyst-bed model is based is given in the Appendix, along with the rate constants that were calculated for a reaction temperature of 600°C. The modeling results for the purely gas phase, homogeneous reactions for partial oxidation of methane are consistent with those in the literature (3,4,5). Table 2 shows the conversions and selectivities for partial oxidation of methane at various residence times, and at 600°C and 0.1 MPa the conversion of methane in the gas phase did not exceed 1% until the residence time at this temperature approached 50 sec. This results because at this relatively low temperature the rates for the gas phase free radical reactions are small, making it necessary for longer residence times to be employed during which the gas phase free radicals accumulate in the system so that secondary reactions can occur.

Although the selectivity to formaldehyde is appreciable, particularly at shorter residence times, the calculated selectivity to methanol is zero. However, one cannot conclude, based on such an observation, that methanol is not produced in the gas phase methane oxidation process because this result could be caused by a higher rate of methanol decomposition than the rate of methanol production. This possibility was investigated by removing all of the elementary steps for methanol decomposition from the model, thus cutting off all of the possible pathways for methanol disappearance. Computations carried out with this abbreviated model showed that there was still no methanol predicted in the product mixture. Therefore, the gas phase kinetic model indicates that methanol cannot be produced by the gas phase partial oxidation of methane. Since methanol is excluded from the precursors for formaldehyde formation, upon consulting the list of reactions in the Appendix, one can see that formaldehyde would be formed from the direct reaction of methyoxide with various gas phase free radicals.

Table 2. Calculated methane conversions and product selectivities for the gas phase partial oxidation of methane as a function of the residence time using a CH_4/Air = 1.5 reactant mixture at 600°C and 0.1 MPa.

Residence Time (sec)	CH_4 Conv. (mol%)	Product Selectivities (mol%)					
		C_2H_4	C_2H_6	CO_2	CO	CH_2O	CH_3OH
0.30	≈0.000	0.0	10.0	0.0	0.2	87.9	0.0
0.50	≈0.000	0.0	10.2	0.0	0.4	82.0	0.0
0.80	0.001	0.0	10.9	0.0	0.7	81.6	0.0
1.00	0.001	0.0	11.4	0.0	0.9	82.3	0.0
1.50	0.002	0.0	12.6	0.0	1.4	85.0	0.0
2.00	0.002	0.0	13.2	0.0	2.0	83.7	0.0
3.00	0.004	0.0	14.4	0.0	3.3	81.0	0.0
4.00	0.006	0.0	15.8	0.0	4.8	78.3	0.0
6.00	0.012	0.1	19.0	0.0	8.4	72.2	0.0
10.00	0.033	0.3	26.1	0.0	17.4	55.9	0.0
30.00	0.512	5.1	41.1	0.3	43.8	9.6	0.0
50.00	1.309	11.4	37.3	0.9	46.3	3.9	0.0
90.00	3.716	20.9	27.9	2.7	46.6	1.7	0.0

At near-zero conversion of methane (at short residence times), formaldehyde was the principal product formed, along with a smaller quantity of ethane, and this indicates that these two products were primary products. As the residence time increased, the CO_x (mainly CO) selectivity increased. This is consistent with CO being formed as a secondary product from formaldehyde. Ethane was also a primary product, but its selectivity increased rather than decreased with methane conversion, at least up to 30 sec as shown in Table 2. The difference in the selectivity pattern between CH_2O and C_2H_6 is due to the requirement that C_2H_6 formation requires the reaction of two methyl radicals while formaldehyde formation only requires one radical and one gas phase molecule (O_2), which has a large concentration at low methane conversion levels but a very low concentration at high methane conversion levels where the concentration of CH_3 radicals is high.

It was also of interest to investigate the effect of total pressure on the conversion of methane and the oxygenate yields. In order to avoid oxygen-limiting conditions, the calculation was carried out at a relatively short residence time of 5 sec. The resulting methane conversions and formaldehyde percentage yields are plotted against the total reagent pressure in Figure 2.

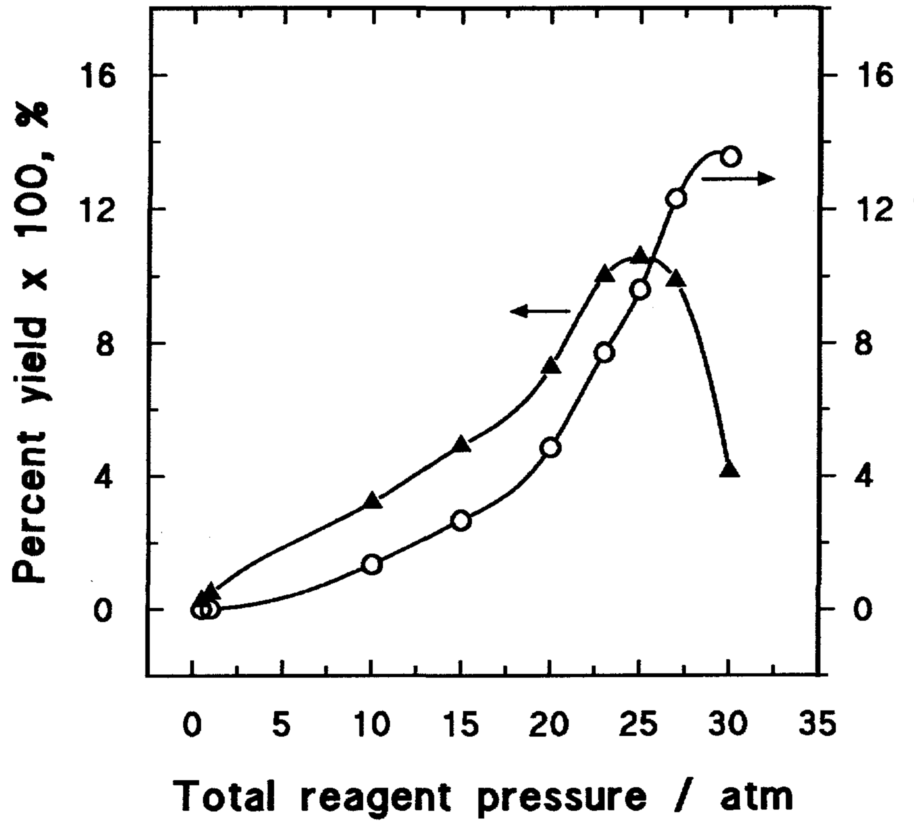

Figure 2. Calculated conversion of methane and %yield of formaldehyde as a function of total reaction pressure of CH_4/Air = 1.5 with a residence time of 5 sec at 600°C.

As indicated by the figure, the conversion of methane steadily increased as the total pressure increased up to 3.0 MPa (30 atm), where it began to level off because the supply of unreacted oxygen was becoming limited. This reflects the enhanced free radical reactions due to increased pressure. However, at the reaction pressure was increased, the %yield of formaldehyde did not smoothly increase with pressure. The %yield of CH_2O reached a maximum at about 2.5 MPa and then sharply dropped, probably because the increased gas phase radical concentration greatly increased the reactions for formaldehyde removal and enhanced C_2 hydrocarbon formation. This indicates that under a given set of reaction conditions, there is a limit for formaldehyde yield *via* purely gas phase reactions.

Conclusions

Kinetics modeling of chemical reaction systems is a useful tool in understanding the mechanisms and limitations of reactions. In contrast to heterogeneous catalysis where a lack of known rate constants for surface reactions can frustrate kinetic analyses, the database of rate constants for gas phase reactions is fairly extensive and reliable. The results in this report clearly demonstrated this point and provided insight into several areas of interest in the partial oxidation of methane to oxygenates.

The extent to which an external source of methyl radicals could contribute to the formation of oxygenates is limited by the fast decay of methyl radical concentration along the reaction pathway. In any practical reactor system, the modeling showed that at most only a few percent of the methyl radicals generated in one catalyst bed could actually arrive at the subsequent second catalyst layer to undergo further reaction.

Contrary to some literature proposals, by the model utilized here predicted that methanol is not a *gas phase* product under the experimental conditions considered, indicating the importance of surface involvement in the process. Formaldehyde, however, can be a gas phase product, and it appears that the presence of a surface usually has a detrimental effect on it. Therefore, inroducing a catalyst may increase the relative yield of methanol as compared to that of formaldehyde by enhancing both CH_3OH formation and CH_2O decomposition or oxidation. The total yield of oxygenates may either benefit or suffer, depending on the particular experimental conditions.

APPENDIX

GAS-PHASE REACTIONS IN THE KINETIC MODEL FOR METHANE OXIDATION

	Reaction	Rate constant at 600°C
1	$OH+H_2=H_2O+H$	1.56e+12
2	$H+HO_2=OH+OH$	1.10e+14
3	$H+O_2=HO_2$	1.24e-13
4	$H+H_2O=OH+H_2$	3.79e+09
5	$H+O_2=OH+O$	6.37e+10
6	$OH+O=H+O_2$	1.37e+13
7	$O+H_2=OH+H$	1.58e+11
8	$OH+H=O+H_2$	1.94e+11
9	$OH+OH=H_2O+O$	4.19e+12
10	$OH+M=O+H+M$	1.44e-06
11	$HO_2+H_2=H_2O_2+H$	8.29e+07
12	$HO_2+M=O_2+H+M$	1.54e+05
13	$HO_2+H_2=H_2O_2+H$	8.29e+07
14	$HO_2+M=O_2+H+M$	1.54e+05
15	$HO_2+HO_2=H_2O_2+O_2$	1.81e+12
16	$OH+OH=H_2O_2$	1.07e-13
17	$O+H_2O=OH+OH$	8.34e+09
18	$H+HO_2=H_2+O_2$	2.33e+13
19	$OH+HO_2=H_2O+O_2$	1.41e+13
20	$O+HO_2=OH+O_2$	2.12e+13
21	$OH+O_2=O+HO_2$	1.26e+02
22	$H_2O_2+H=HO_2+H_2$	9.66e+11
23	$H_2O_2+H=H_2O+OH$	3.41e+12
24	$H_2O_2+OH=H_2O+HO_2$	1.49e+12
25	$H_2O_2+O=HO_2+OH$	1.43e+12
26	$H_2O_2+N2=OHOH+N2$	1.28e+07
27	$H_2O_2+M=OHOH+M$	1.31e+07
28	$H_2O_2+H_2O=OHOH+H_2O$	1.31e+08
29	$H_2O_2+O=OH+HO_2$	1.36e+06
30	$H_2O_2+O_2=HO_2+HO_2$	1.76e+05
31	$CH_4+O_2=CH_3+HO_2$	2.82e+01
32	$CH_4+OH=CH_3+H_2O$	9.99e+11
33	$CH_4+O=CH_3+OH$	4.87e+11

34	$CH_4+H=CH_3+H_2$	3.24e+11
35	$CH_4+HO_2=CH_3+H_2O_2$	1.94e+07
36	$CH_4=CH_3+H$	2.49e-07
37	$CH_4+CH_3O=CH_3OH+CH_3$	2.02e+09
38	$CH_3+CH_3=C_2H_6$	2.40e+13
39	$CH_3+O_2=CH_2O+OH$	6.58e+08
40	$CH_3+O_2=CH_3O_2$	1.38e+10
41	$CH_3+O_2=CH_3O+O$	2.13e+07
42	$CH_3+N2O=CH_3O+N2$	8.72e+08
43	$CH_3+OH=CH_3OH$	1.49e+13
44	$CH_3+HO_2=CH_4+O_2$	3.61e+12
45	$CH_3+HO_2=CH_3O+OH$	1.99e+13
46	$CH_3+H=CH_4$	7.53e+13
47	$CH_3+O=CH_2O+H$	7.83e+13
48	$CH_3+CH_2O=CH_4+CHO$	8.90e+10
49	$CH_3+CHO=CH_4+CO$	1.20e+14
50	$CH_3+CHO=CH_3CHO$	1.81e+13
51	$CH_3+H_2O=CH_4+OH$	1.73e+08
52	$CH_3+H_2=CH_4+H$	9.80e+09
53	$CH_3+C_2H_4=CH_4+C_2H_3$	1.77e+09
54	$CH_3O+M=CH_2O+H+M$	4.16e+17
55	$CH_3O+O_2=CH_2O+HO_2$	1.84e+10
56	$CH_3O+H=CH_2O+H_2$	1.99e+13
57	$CH_3O+O=CH_2O+OH$	6.02e+12
58	$CH_3O+OH=CH_2O+H_2O$	1.81e+13
59	$CH_3O+HO_2=CH_2O+H_2O_2$	3.01e+11
60	$CH_3O+CH_2O=CH_3OH+CHO$	2.36e+10
61	$CH_3O+CO=CH_3+CO_2$	4.71e+10
62	$CH_3O+CHO=CH_3OH+CO$	9.03e+13
63	$CH_3O+CH_3=CH_2O+CH_4$	2.41e+13
64	$CH_3O+C_2H_3=CH_2O+C_2H_4$	2.41e+13
65	$CH_3O_2+M=CH_3+O_2M$	6.27e+11
66	$CH_3O_2+H_2=CH_3O_2H+H$	8.29e+07
67	$CH_3O_2+H=CH_3O+OH$	9.63e+13
68	$CH_3O_2+O=CH_3O+O_2$	9.63e+12
69	$CH_3O_2+OH=CH_3OH+O_2$	6.02e+13
70	$CH_3O_2+HO_2=CH_3O_2H+O_2$	1.65e+11
71	$CH_3O_2+H_2O_2=CH_3O_2H+HO_2$	1.82e+10
72	$CH_3O_2+CH_4=CH_3O_2H+CH_3$	2.04e+07
73	$CH_3O_2+C_2H_6=CH_3O_2H+C_2H_5$	1.90e+08

75	$CH_3O_2+CH_3=CH_3O+CH_3O$	2.41e+13
76	$CH_3O_2+CH_3O_2=2CH_3O+O_2$	2.05e+11
77	$CH_3OH+H=CH_3O+H_2$	2.00e+12
78	$CH_3OH+OH=CH_3O+H_2O$	4.34e+12
79	$CH_3OH+O=CH_3O+OH$	9.98e+11
80	$CH_3OH+M=CH_3+OH+M$	5.01e+02
81	$CH_3CHO+O=CH_3CO+OH$	2.07e+12
82	$CH_3CHO+H=CH_3CO+H_2$	5.05e+12
83	$CH_3CHO+OH=CH_3CO+H_2O$	9.99e+12
84	$CH_3CO+M=CH_3+CO+M$	2.53e+12
85	$CH_2O+H=H_2+CHO$	1.07e+13
86	$CH_2O+O=CHO+OH$	1.37e+13
87	$CH_2O+OH=CHO+H_2O$	1.52e+13
88	$CH_2O+HO_2=CHO+H_2O_2$	6.87e+10
89	$CH_2O+O=CO_2+H+H$	1.37e+13
90	$CH_2O+O_2=HO_2+CHO$	9.82e+04
91	$CHO+H=CO+H_2$	2.00e+14
92	$CHO+M=H+CO+M$	8.04e+10
93	$CHO+OH=CO+H_2O$	3.01e+13
94	$CHO+M=H+CO+M$	8.04e+10
95	$CHO+O_2=HO_2+CO$	2.23e+13
96	$CHO+HO_2=OH+H+CO_2$	3.01e+13
97	$CO+OH=CO_2+H$	2.07e+11
98	$CO+HO_2=CO_2+OH$	1.34e+09
99	$CO+O_2=CO_2+O$	1.65e+02
100	$CO_2+H=CO+OH$	3.41e+08
101	$CO_2+O=CO+O_2$	9.53e+01
102	$2CH_3O=CH_3O+CH_3O$	6.02e+18
103	$CH_3O_2H=CH_3O+OH$	6.02e+18
104	$C_2H_6=CH_3+CH_3$	4.57e-03
105	$C_2H_6=C_2H_5+H$	3.39e-06
106	$C_2H_6+O_2=C_2H_5+HO_2$	5.49e+02
107	$C_2H_6+H=C_2H_5+H_2$	1.50e+12
108	$C_2H_6+O=C_2H_5+OH$	2.11e+12
109	$C_2H_6+OH=C_2H_5+H_2O$	4.77e+12
110	$C_2H_6+HO_2=C_2H_5+H_2O_2$	1.90e+08
111	$C_2H_6+CH_3=C_2H_5+CH_4$	1.02e+10
112	$C_2H_6+CH_3O=CH_3OH+C_2H_5$	7.35e+09
113	$C_2H_5+H=C_2H_4+H_2$	1.81e+12
114	$C_2H_5+H=CH_3+CH_3$	3.00e+13

115	$C_2H_5+O=CH_3CHO+H$	8.01e+13
116	$C_2H_5+HO_2=C_2H_4+H_2O_2$	3.01e+11
117	$C_2H_5+HO_2=C_2H_6+O_2$	3.01e+11
118	$C_2H_5+OH=C_2H_4+H_2O$	2.41e+13
119	$C_2H_5+M=C_2H_4+H+M$	2.31e+10
120	$C_2H_5+O_2=C_2H_4+HO_2$	1.71e+11
121	$C_2H_5+H_2=C_2H_6+H$	6.33e+09
122	$C_2H_5+CH_2O=C_2H_6+CHO$	8.82e+10
123	$C_2H_5+C2H_5=C_2H_6+C_2H_4$	1.39e+12
124	$C_2H_5+CHO=C_2H_6+CO$	1.20e+14
125	$C_2H_5+H_2O_2=C_2H_6+HO_2$	5.41e+09
126	$C_2H_5+CH_4=C_2H_6+CH_3$	5.16e+08
127	$C_2H_4+O_2=C_2H_3+HO_2$	2.07e+01
128	$C_2H_4+OH=C_2H_3+H_2O$	3.81e+11
129	$C_2H_4+OH=CH_3+CH_2O$	6.22e+12
130	$C_2H_4+O=CH_3+CHO$	4.97e+12
131	$C_2H_4+H=C_2H_3+H_2$	1.33e+11
132	$C_2H_4+H=C_2H_5$	1.58e+13
133	$C_2H_4+HO_2=CH_3CHO+OH$	1.21e+08
134	$C_2H_4+C_2H_5=C_2H_6+C_2H_3$	2.37e+08
135	$C_2H_3+OH=CH_3CHO$	3.01e+13
136	$C_2H_3+CHO=C_2H_4+CO$	9.03e+13
137	$C_2H_3+CH_2O=C_2H_4+CHO$	8.70e+10
138	$C_2H_3+CH_4=C_2H_4+CH_3$	1.23e+11
139	$C_2H_3+O=CH_2CO+H$	9.63e+13
140	$C_2H_3+H_2O_2=C_2H_4+HO_2$	1.61e+10
141	$C_2H_3+H_2O=C_2H_4+OH$	1.73e+08
142	$C_2H_3+HO_2=CH_3+OH+CO$	3.01e+13
143	$C_2H_3+H_2=C_2H_4+H$	3.72e+10
144	$C_2H_3+H=C_2H_2+H_2$	9.63e+13
145	$C_2H_3+M=C_2H_2+H+M$	2.22e+09
146	$C_2H_2+OH=C_2H+H_2O$	4.53e+09
147	$C_2H_2+H=C_2H+H_2$	1.06e+09
148	$C_2H_2+H=C_2H_3$	1.68e+12
149	$C_2H_2+CH_3=C_2H+CH_4$	3.67e+07
150	$C_2H_2+O_2=CHO+CHO$	1.46e-03
151	$C_2H_2+O=CO+CH_2$	5.82e+12
152	$C_2H_2+H=C_2H_3$	2.78e-12
153	$C_2H_2+H_2=C_2H_4$	1.44e+03
154	$CH_2CO+OH=CH_2O+CHO$	9.99e+12

155	$C_2H+O_2=CO+CHO$	2.41e+12
156	$C_2H+H_2=C_2H_2+H$	2.77e+12
157	$C_2H+OH=C_2H_2+O$	1.81e+13
158	$C_2H+OH=CH_2+CO$	1.81e+13
159	$C_2H+HO_2=C_2H_2+O_2$	1.81e+13
160	$CH_2+O_2=CO+H_2O$	2.41e+11

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