AN EXTENDED KINETIC MODEL AND ITS REDUCTION BY SENSITIVITY ANALYSIS FOR THE METHANOL/OXYGEN GAS-PHASE THERMOLYSIS

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Thermolysis of methanol in the presence of oxygen was investigated by computational modelling and sensitivity analysis in the temperature interval 900 K $\leq T \leq$ 1100 K and at reaction times 10^{-5} s $\leq t \leq$ 1 s. Based on earlier experimental investigations and new kinetic data, a complex mechanism was set up to clarify the formation of formaldehyde, glycol, carbon monoxide, water, acetaldehyde, and formic acid, and the role of the radicals CH_2OH, CH_3, CHO, C_2H_3O, H, and O in the kinetic process. The resulting mechanism of 48 reactions and 20 species was reduced to 32 reactions and 17 species at 900 K and to 31 reactions and 17 species at 1000 K and at 1100 K. The results of simulations were compared to the experimentally measured concentrations of the pyrolytic products.

Introduction and experimental background

The thermolysis of the gas system $CH_3OH/O_2/Ar$ has been investigated experimentally [1,2] in a flow quartz-tube reactor in the temperature range 900 K to 1100 K, and at CH_3OH/O_2 ratios from 4:1 to 16:1. The main stable products were formaldehyde H_2CO, glycol $(CH_2OH)_2$, carbon monoxide and water. A series of experiments were carried out to maximize the yield of $(CH_2OH)_2$ and these experiments showed that the optimal formation of glycol occurred at the temperature of 1000 K for a mixture of $CH_3OH : O_2$ = 8:1 after reaction time $t = 0.2 - 0.3$ s.

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Simulations of the methanol-oxygen thermolysis using a few-step kinetic model [1,2] reproduced only some of the essential results, for example the distribution of the main stable products H_2CO, H_2O and CO. It was shown that, at these experimental conditions, the hydrogen abstraction channel, $CH_3OH + O_2 \rightarrow CH_2OH + HO_2$, and the further reactions of CH_2OH, HO_2, OH, and H_2O_2 were of essential importance for the formation of the final products.

However, some questions remained unanswered. Simulation results showed deviations from the experimental measurements for (CH_2OH) by about 20%. Small amounts (<1 mol%) of acetaldehyde, CH_3CHO, and formic acid, $HCOOH$, were found. This lead to the assumption that radicals CH_3, CHO, H, and O have kinetic significance at these low temperatures as well. Note, that it has been well known that at temperatures above 1200 K the decomposition of methanol, $CH_3OH \rightarrow CH_3 + OH$, and the methyl radical reactions play an important role in methanol thermolysis [3,4].

An extended mechanism, taking into consideration the stable products, CH_3CHO, $HCOOH$, CH_4 , and the radicals CH_3, CHO, C_2H_3O, O, and H, was formulated for the explanation of the thermolysis at temperatures up to 1100 K. The significance of these species and reactions was investigated by program package KINAL. The aims of the present study were:
– Explanation of the qualitative and quantitative experimental data for glycol and minor products in the CH_3OH/O_2 thermolysis reaction at 1000 K by model calculations using an extended reaction mechanism. Investigation of the product distribution in the temperature range 900 K – 1100 K.
– Explanation of the role and kinetic significance of radicals CH_3, CHO, C_2H_3O, O, and H in the temperature range 900 – 1100 K.
– Reduction of the number of species and reactions of the mechanism without a significant change of the important product concentrations.

Computational methods

According to a recent article [5], all species of a reaction mechanism can be classified into three categories: important, necessary and redundant species. The accurate reproduction of the experimental data for important species is the aim of the model calculations. The remaining non-important species are either necessary or redundant, that is the calculation of the concentrations of them are or are not required, respectively, for the calculation of the concentration of important species. A species is redundant if the elimination of all of its consuming reactions does not

cause significant deviation from the solution of the full model regarding important species. In case of species having a low concentration, formed by fast reversible reactions, the elimination of all of its consuming reactions may cause a significant deviation of the concentrations of important species, even if this species is redundant. Therefore the simultaneous elimination of consuming and fast producing reactions has to be tried as well.

Two kinds of reaction importance can be distinguished [6]. A reaction has a high tuning importance if a small change of its rate parameter alters significantly the results of the model. A wider set of reactions have high reduction importance, i.e., they can not be eliminated from the mechanism without significant changes in the modelling results.

Reaction importance in the second sense can be identified by the investigation of the rate sensitivity matrix F [7], where $F = \{ \partial \ln f_i / \partial \ln k_j \}$, i refers to the indices of important and necessary species, f_i is the rate of production of species i, and k_j is the j-th rate coefficient. Important reactions can be detected by the principal component analysis [8] of matrix F, i.e., the eigenvalue-eigenvector decomposition of matrix $F^T F$, as they appear as significant elements of eigenvectors having high eigenvalues. Note, that the applications of sensitivity methods for the analysis of reaction mechanisms was reviewed recently [6].

Calculations were carried out by program package KINAL [9]. KINAL generates the differential equations from the chemical mechanism, solves them numerically, identifies the redundant species, determines the rate sensitivity coefficients and carries out the principal component analysis. Finally, KINAL gives a recommendation for a reduced mechanism and calculates the differences between the full and the reduced models.

Results of the analysis

Table I summarizes the reaction steps and the corresponding rate data of the extended mechanism of 20 species and 48 reactions for the methanol/oxygen thermolysis. The core of the mechanism (reactions R1–R19, R26 and R27) is identical to our previous kinetic considerations [2] and it has been extended by reactions of species CH_3CHO, CH_4, CH_3, C_2H_3O and O. The previous mechanism was based on the evaluated data of Warnatz [10]. Recently, a new set of evaluated data of Baulch et al. [13] became available and whenever possible these data were used. Kinetic data for some reactions of our mechanism were not present in Ref. [13]

and the up-to-date data [11,12,14–16] for these reactions were found in the NIST Chemical Kinetics Data Base [17].

Table I

Reaction mechanism for the methanol/oxygen thermolysis

No.	Reaction	lg A	N	E_A	Ref.
1	$CH_3OH + O_2 = CH_2OH + HO_2$	13.3	0.0	44.9	[11]
2	$CH_3OH + Ar = CH_2OH + H + Ar$	14.0	0.0	93.3	[10]
3	$CH_3OH + H = CH_2OH + H_2$	13.6	0.0	6.1	[10]
4	$CH_3OH + HO_2 = CH_2OH + H_2O_2$	11.0	0.0	12.6	[11]
5	$CH_3OH + OH = CH_2OH + H_2O$	12.7	0.0	1.4	[12]
6	$CH_2OH + H_2O_2 = CH_3OH + HO_2$	9.5	0.0	2.6	[11]
7	$CH_2OH + O_2 = H_2CO + HO_2$	*			[13]
8	$CH_2OH + Ar = H_2CO + H + Ar$	14.8	0.0	29.6	[14]
9	$H_2CO + O_2 = CHO + HO_2$	13.3	0.0	38.9	[15]
10	$H_2CO + HO_2 = CHO + H_2O_2$	12.3	0.0	11.7	[15]
11	$H_2CO + H = CHO + H_2$	14.0	0.0	4.9	[16]
12	$CHO + O_2 = CO + HO_2$	12.5	0.0	0.0	[13]
13	$2CH_2OH = (CH_2OH)_2$	13.0	0.0	0.0	[11]
14	$2HO_2 = H_2O_2 + O_2$	12.3	0.0	1.6	[13]
15	$H_2O_2 + Ar = 2OH + Ar$	16.2	0.0	43.2	[13]
16	$OH + HO_2 = H_2O + O_2$	13.5	0.0	0.5	[13]
17	$(CH_2OH)_2 = 2CH_2OH$	**			[1]
18	$CH_2OH + HO_2 = HCOOH + H_2O$	16.4	0.0	47.4	[2]
19	$CHO + OH = H_2O + CO$	14.0	0.0	0.0	[13]
20	$CH_3CHO = CH_3 + CHO$	15.8	0.0	82.2	[13]
21	$CH_3 + CHO = CH_3CHO$	13.2	0.0	0.0	[15]
22	$CH_3OH + Ar = CH_3 + OH + Ar$	16.3	0.0	91.8	[11]
23	$2CH_2OH = CH_3OH + H_2CO$	12.7	0.0	0.0	[11]
24	$H_2CO + OH = CHO + H_2O$	13.5	0.0	1.2	[10]
25	$CHO + H = CO + H_2$	14.0	0.0	0.0	[13]
26	$HCOOH + Ar = CHO + OH + Ar$	***			
27	$CHO + OH = HCOOH$	11.0	0.0	0.0	[2]
28	$CH_3OH + CH_3 = CH_2OH + CH_4$	11.4	0.0	9.8	[10]
29	$CH_4 + OH = CH_3 + H_2O$	7.2	1.8	2.8	[13]
30	$H_2CO + CH_3 = CHO + CH_4$	12.6	0.0	8.9	[13]
31	$H + HO_2 = 2OH$	14.2	0.0	0.9	[13]
32	$CH_3CHO + H = C_2H_3O + H_2$	9.6	1.2	2.4	[13]
33	$CH_3CHO + OH = C_2H_3O + H_2O$	10.4	0.7	1.1	[13]
34	$CH_3CHO + CH_3 = C_2H_3O + CH_4$	-5.7	5.6	2.5	[13]
35	$C_2H_3O + Ar = CH_3 + CO + Ar$	17.0	0.0	15.6	[13]
36	$HO_2 + H = H_2 + O_2$	13.6	0.0	1.4	[13]
37	$O_2 + H + Ar = HO_2 + Ar$	17.0	-0.8	0.0	[13]
38	$CH_3 + O_2 = CH_2OH + O$	14.1	0.0	31.6	[13]
39	$CH_3OH + O = CH_2OH + OH$	13.0	0.0	4.7	[10]
40	$CH_4 + O = CH_3 + OH$	9.0	1.6	8.5	[13]
41	$CH_4 + H = CH_3 + H_2$	4.1	3.0	8.1	[13]
42	$CH_3 + H + Ar = CH_4 + Ar$	14.1	-0.4	0.0	[13]
43	$CH_3 + O = H_2CO + H$	13.9	0.0	0.0	[13]
44	$H_2CO + O = CHO + OH$	11.6	0.6	2.8	[13]
45	$CHO + O = CO + OH$	13.5	0.0	0.0	[13]
46	$HO_2 + O = OH + O_2$	13.5	0.0	0.0	[13]
47	$CH_3CHO + O = C_2H_3O + OH$	12.8	0.0	1.8	[13]
48	$C_2H_3O + H = CH_3CHO$	13.3	0.0	0.0	[10]

* $k_7 = 1.6 \times 10^{15} T^{-1.0} + 7.2 \times 10^{13} \exp(-1800/T)$; ** $lg\, k_{17} = 15.7 - 19150/T$; *** $lg\, k_{26} = 22.4 - 16420/T$;
The rate coefficients are given in the form $k_j = AT^N \exp(-E_A/RT)$ and E_A in kcal mol^{-1},
T in K, A in cm^3 mol^{-1} s^{-1}.

The reaction mechanism was analyzed at three temperatures: $T=900$ K, 1000 K and 1100 K. The initial concentrations were $[Ar] = 1.02 \times 10^{-5}$ mol cm^{-3}, $[CH_3OH]_0 = 1.76 \times 10^{-6}$ mol cm^{-3} and $[O_2] = 2.20 \times 10^{-7}$ mol cm^{-3} i.e., $CH_3OH : O_2 = 8 : 1$. The stable products of the thermolysis, H_2CO, H_2O, CO, $(CH_2OH)_2$, CH_3CHO and HCOOH, were considered as important species. The maximum concentration of the products, corresponding to about 25% methanol conversion, was reached at 1 s, 0.2–0.3 s, and 0.05–0.1 s, at 900 K, 1000 K, and 1100 K, respectively.

As a first step, redundant species were searched for. As H_2 is not an important species and the mechanism contains H_2 producing steps only, H_2 can be considered a redundant species without further analysis. Raw material CH_3OH was considered as necessary without investigation as well. Determination of redundant species was carried out by the method of reduced models [5], briefly described above. The results were summarized in Table II. Large deviations (indicated by the letter L) meant that at reaction times up to 1 s the deviation between the reduced and the full model is greater than 1% for H_2CO, H_2O, CO, $(CH_2OH)_2$ and greater then 10% for CH_3CHO and HCOOH. Experimental uncertainties were much higher for the low-

Table II

Identification of redundant species by the method of reduced models.

Species	Consuming steps omitted at the temperature			Consuming and producing steps omitted at the temperature			Decision
	900 K	1000 K	1100 K	900 K	1000 K	1100 K	
CH_3OH	L	L	L	L	L	L	necessary
O_2	L	L	L	L	L	L	necessary
CH_2OH	L	L	L	L	L	L	necessary
HCO	L	L	L	L	L	L	necessary
HO_2	L	L	L	L	L	L	necessary
H_2O_2	L	L	L	L	L	L	necessary
OH	L	L	L	L	L	L	necessary
H	L	L	L	L	L	L	necessary
CH_3	L*	L	L	L*	L	L	necessary
CH_4	S	S	S	–	–	–	redundant
C_2H_3O	L*	L*	S	S	S	–	redundant
O	S	S	S	–	–	–	redundant
H_2	–	–	–	–	–	–	redundant

L and S denote large and small deviation, respectively, in the calculated concentration of important species. L* denotes large deviation in the calculated concentration of CH_3CHO only

concentration CH_3CHO and HCOOH, hence a less strict accuracy level was required for them. Small deviations were indicated by the letter S. The results showed that species CH_2OH, H_2O_2, HO_2, OH, CHO, H and CH_3 were necessary and species CH_4, C_2H_3O, and O were redundant at all the three temperatures. Note, that at 900 K CH_3 was necessary for the formation of CH_3CHO only.

Table III

*Importance of reactions at several reaction times and temperatures
as identified by the principal component analysis of matrix* **F**

No.	1×10^{-5}	1×10^{-4}	1×10^{-3}	Reaction time [s] 5×10^{-2}	1×10^{-1}	5×10^{-1}	1
5	▨▨▉	▨▨▉	▨▨▉	▨▨▉	▨▨▉	▨▨▉	▨▨▉
7	▨▨▉	▨▨▉	▨▨▉	▨▨	▨▨	▨	
8				▉	▉	▨▉	▨▨▉
10				▨	▨	▨	
11				▉	▉	▨	
12	▨▨▉	▨▨▉	▨▨▉	▨▨	▨▨	▨	
13	▨▨▉	▨▨▉	▨▨▉	▨▨▉	▨▨▉		▨
17					▉	▨▉	▨▉
18	▨▨▉	▨▨▉	▨▨▉	▨▨	▨		
19				▉	▉	▨▉	▨▨▉
20						▉	▉
21	▨▨▉	▨▨▉	▨▨▉	▨▨▉	▨▨▉	▨▨▉	▨▨▉
23							▨▨▉
24				▉	▨▉	▨▨▉	▨▨▉
25				▉	▉	▨▉	▨▨▉
26			▨▉		▨▉	▨▉	▨▨▉
27			▨▉	▨▉	▨▨▉	▨▉	▨▨▉
33				▨			▨
35						▉	▉

Significant reactions are denoted by ▨, ▨ and ▉ at 900 K, 1000 K and 1100 K, respectively

Redundant reactions were identified by the principal component analysis of the rate sensitivity matrices at reaction times 10^{-5} s, 10^{-4} s, 10^{-3} s, 10^{-2} s, 0.1 s, 0.5 s and 1 s, considering important and necessary species only. A reaction was considered

to be important if it belonged to an eigenvector element greater then 0.1 of a principal component having an eigenvalue greater then 10^{-4}. Results of principal component analysis are given in Table III.

Reactions R5, R7, R8, and R24 were of great importance for the formation of H_2CO. Formation of CO and $(CH_2OH)_2$ was determined by reactions R12 and R13. Reactions R18, R26, and R27 were important for the formation of HCOOH and reaction R21 ruled the formation of CH_3CHO. Reactions R10, R17, R20, R33, and R35 were of importance at times greater than 5×10^{-2} s only. The obtained reduced mechanisms consisted of 32 reactions at 900 K (reactions R1, R3–R33) and 31 reactions at 1000 K and at 1100 K (reactions R1–R5, R7–R17, R19, R22–R35).

As the small amount of CH_3CHO and HCOOH found experimentally may not be the product of the thermolysis at near 1000 K (see discussion later), the whole procedure was repeated considering H_2CO, H_2O, CO and $(CH_2OH)_2$ as important species only. In this case the necessary species were the same and at 1000 K the mechanism could be reduced by principal component analysis to 24 reactions of 15 species (reactions R1–R5, R7–R17, R19, R22–R25, R28, R30, and R31).

Table IV shows that the deviation of the concentrations of the important species, calculated from the full and reduced models were negligible.

Table IV

Deviation (%) of the concentration of important species derived from the full and reduced models

Species	Red. model 31r, 17c		T = 1000 K Red. model 24r, 15c		T = 900 K Red. model 32r, 17c	
	$t = 0.1$ s	$t = 0.5$ s	$t = 0.1$ s	$t = 0.5$ s	$t = 0.1$ s	$t = 0.5$ s
H_2CO	0.002	0.130	0.001	0.081	−0.004	0.001
H_2O	−0.001	0.001	−0.003	0.001	−0.004	−0.001
CO	0.001	−0.057	−0.001	−0.038	−0.004	0.003
$(CH_2OH)_2$	0.012	0.313	−0.018	0.317	−0.012	0.001
HCOOH	0.009	−0.153	–	–	−0.035	0.003
CH_3CHO	0.037	−0.061	–	–	0.040	−5.763

Figure 1 shows the concentration-time curves calculated from the reduced mechanisms. The agreement seemed to be satisfactory with the experimental results for species H_2CO, $(CH_2OH)_2$, H_2O, and CO, taking into account the experimental uncertainties as well. At 1000 K the measured concentration of CH_3CHO was much higher than the calculated one, but the former was almost equal to the sum of the calculated CH_3CHO and CHO concentrations. Our conclusion was that most of the

measured CH_3CHO had been formed during the cooling of the gas mixture by reactions of the radical CHO. Probably the small amounts of HCOOH found experimentally were also formed during the cooling of the mixture.
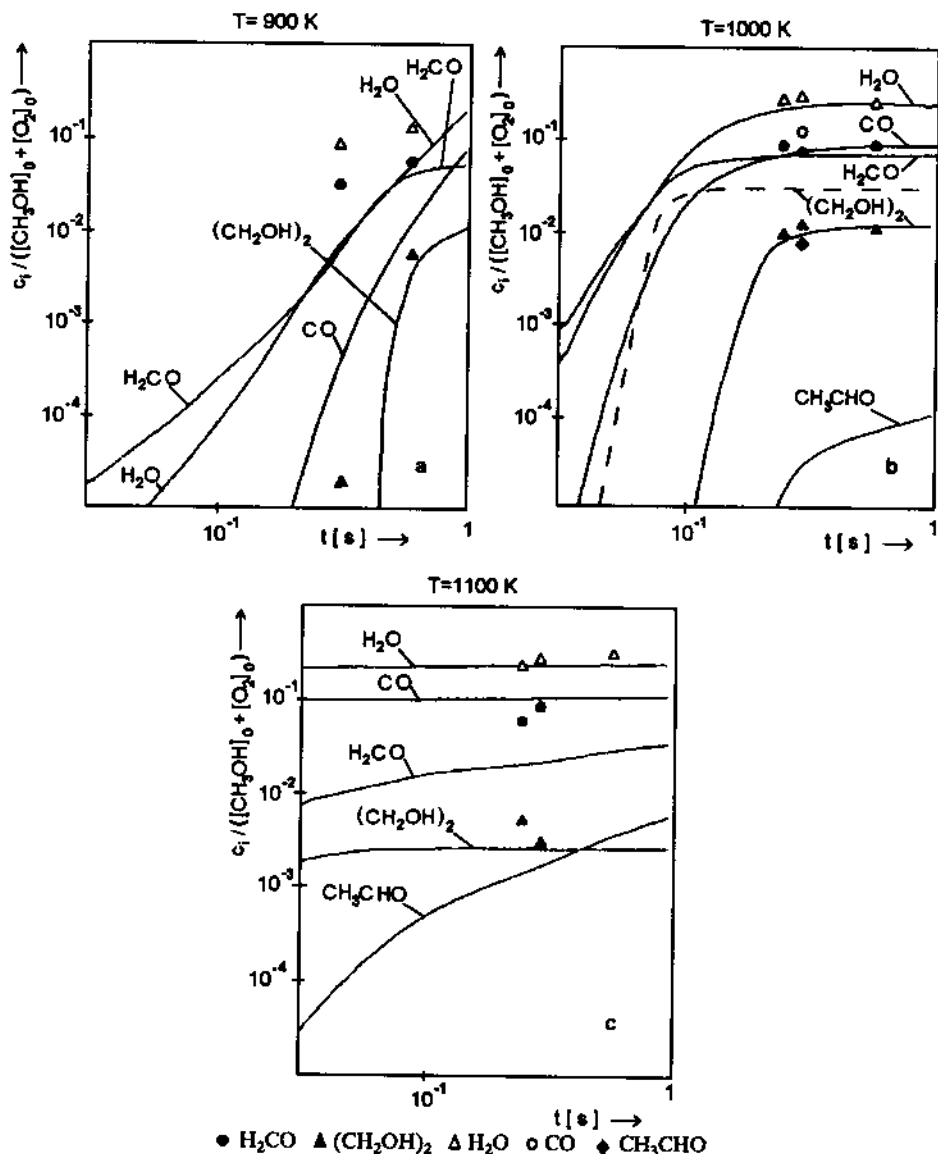

Fig. 1. Experimental results (see legends) and concentration-time curves, calculated from the reduced mechanisms, for the methanol-oxygen thermolysis system at three temperatures. The dashed line in Fig. 1b indicates the glycol concentration calculated from mechanism published in Ref. [2]

species CH_4, C_2H_3O, and O were redundant for the description of the generation of H_2CO, H_2O, CO, $(CH_2OH)_2$, CH_3CHO, and HCOOH.

Principal component analysis of the rate sensitivity matrices, considering the important and necessary species only, showed that it was possible to reduce the full mechanism to 32 reactions and 17 species at 900 K, and to 31 reactions and 17 species at 1000 K and 1100 K. By neglecting of the minor products CH_3CHO and HCOOH it was possible to reduce the complete mechanism to 24 reactions and 15 components. The deviations between the results of the full and reduced models were negligible.

The comparison of the simulation results to the experimental data showed that the obtained reduced models described well the generation of H_2CO, $(CH_2OH)_2$, H_2O, and CO. Our conclusion was that most of the CH_3CHO, and HCOOH found experimentally had been generated during the cooling of the hot product gas mixture.

Acknowledgement

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In Figure 1b the glycol concentration calculated from the 21-step mechanism published in [2] is also marked by dashed line. Although the size of our 24-step reduced mechanism is almost the same, the latter reproduces much better the experimental glycol concentration, as a result of the updating of the rate coefficients, the extension and subsequent reduction of the model. There are 17 common reactions of the two models.

Figure 2 shows the calculated distributions of the radical species at 900 K and 1000 K. At 900 K the reactive intermediates H_2O_2, HO_2, CH_2OH and CHO were formed mainly at reaction times $0.5-1$ s. At 1000 K the radicals H_2O_2, HO_2, CH_2OH reached a maximum near 0.1 s. For reaction times greater than 0.5 s only radicals CHO, CH_2OH, and CH_3 remained in the system.
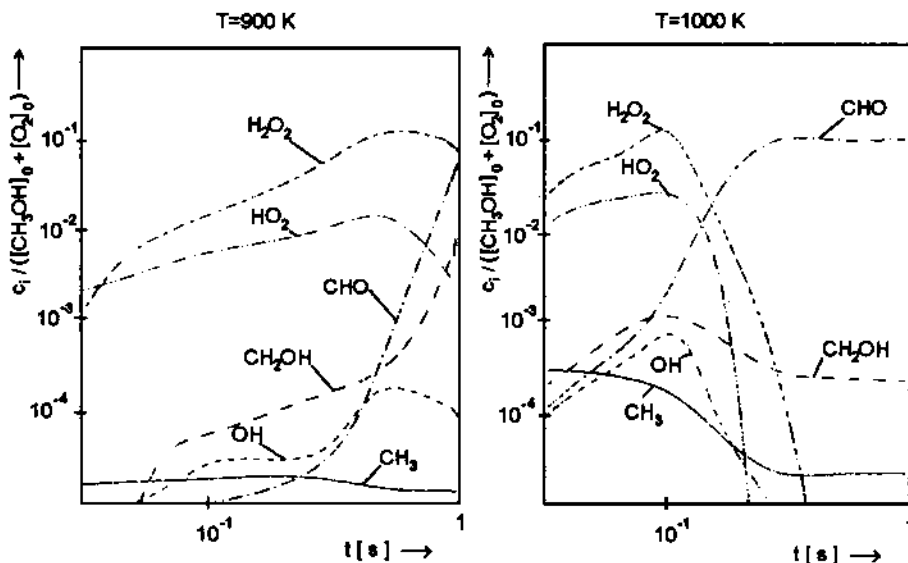

Fig. 2. Calculated concentration of radical species

Conclusions

A 48-step mechanism for the CH_3OH/O_2 thermolysis, which contained the reactions of 20 species, was investigated and reduced. In the temperature range 900 K – 1100 K the calculation of the concentrations of species CH_2OH, H_2O_2, HO_2, OH, CHO, H and CH_3 were necessary and the calculation of the concentrations of