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### Low temperature oxidation of methane: the influence of nitrogen oxides

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# Low temperature oxidation of methane: the influence of nitrogen oxides

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An experimental investigation of methane oxidation in the presence of NO and NO<sub>2</sub> has been made in an isothermal plug-flow reactor at 750–1250K. The temperature for on-set of oxidation was lowered by 250 K in the presence of NO or NO<sub>2</sub> at residence times of 200 ms. At shorter residence times (140 ms) this enhancement effect is reduced for NO but maintained for NO<sub>2</sub>. Furthermore two temperature regimes of oxidation separated by an intermediate regime where only little oxidation takes place exist at residence times of 140 ms, if NO is the only nitrogen oxide initially present. The results were explained by the competition between three reaction paths from CH<sub>3</sub> to CH<sub>2</sub>O. A direct high temperature path (A), a two-step NO<sub>2</sub> enhanced low temperature path (B) and a slow three step NO enhanced path (C), which may produce NO<sub>2</sub> to activate path B. The negative temperature coefficient behaviour was explained by a competition between paths (A) and (C). A previously published reaction set was modified to take these reaction patterns into account.

The processes discussed here presumably occur to some extent in the exhaust of natural gas engines, but conditions may be modified, either to ensure an enhanced activity to oxidize methane in the exhaust, or alternatively to decrease the activity to reduce the production of unwanted intermediates such as formaldehyde.

**Keywords:** NO<sub>x</sub>; HC's and CO; Kinetics of combustion processes; Global rates and mechanisms

## INTRODUCTION

In recent years natural gas engines have become widespread for co-generation of heat and power production in many countries. Natural gas based co-generation plants are supported by the Danish government through a reduced electricity tax due to the lower CO<sub>2</sub> emission from this source of energy. Most of the engines operate as lean burn engines with air to fuel ratios exceeding 2, mainly due to the

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increased electrical efficiency at higher compression ratios available under lean conditions. However, it has been discovered that a significant amount of methane is emitted from such engines (de Wit *et al.*, 1998), and since methane is a potent green house gas this emission is a significant concern. This study is part of a project focussing on the abatement of this methane emission. Our findings are especially important for the understanding of the oxidation processes taking place in the exhaust channel of such engines.

The chemistry of methane oxidation has been thoroughly investigated, *e.g.* through the work of Miller and Bowman (1989), Hunter *et al.* (1994) and Bowman *et al.* (1996). Most of the focus has been on the interactions of methane and oxygen, and the resulting intermediates. The increasing knowledge about this system has facilitated the understanding of related systems such as thermal generation of  $\text{NO}_x$  during combustion (Miller and Bowman, 1989) and the use of gas reburning in the abatement of  $\text{NO}_x$  (Glarborg *et al.*, 1998). The enhancing effect of  $\text{NO}_x$  on low temperature oxidation of methane has been known for some years. The promoting effect of  $\text{NO}_2$  on methane oxidation in static reactor experiments was reported already by Norrish and Wallace (1934) and later confirmed by Ashmore and Preston (1967). Similar effects have been observed at higher temperatures in a number of shock tube studies (Dorko *et al.*, 1975; Dabora, 1975; Slack and Grillo, 1981). Recently Bromly *et al.* (1996) presented flow reactor experiments showing the effect of NO as well as a detailed chemical mechanism, which describes the phenomenon. The sensitizing effect of NO under oxidizing conditions was further confirmed by Rota *et al.* (1998) in jet-stirred reactor experiments. In addition to these studies,  $\text{NO}_x$  sensitized oxidation has been reported for a number of other fuels, including hydrogen (Bromly *et al.*, 1995), carbon monoxide (Glarborg *et al.*, 1995),  $\text{C}_2\text{-C}_5$  hydrocarbons (Bromly *et al.*, 1992; Nelson and Haynes, 1994; Hjuler *et al.*, 1995; Doughty *et al.*, 1997; Rota *et al.*, 1998; Prabhu *et al.*, 1999), and other organic compounds (Hjuler *et al.*, 1995; Alzueta *et al.*, 1999).

The enhancing effect of nitrogen oxides on fuel oxidation may be of significant practical interest. In internal combustion engines the initiation of oxidation takes place at a moderate temperature and presence of nitrogen oxides may conceivably promote autoignition in a knocking engine (Amano and Dryer, 1998). Full or partial oxidation of unburned hydrocarbons in the exhaust of engines may also be increased in the presence of  $\text{NO}_x$ .

These two potential cases of  $\text{NO}_x$  sensitized oxidation are characterized by a very short available reaction time. In the case of a knocking engine operating at a modest 1500 rpm, autoignition becomes irrelevant if more than a maximum 20 ms are needed, since the spark ignition flame front by then will cover the cylinder. The engine exhaust residence time at high temperatures for large stationary

engines will be about 50 ms. For this reason we decided to complement the experiments by Bromly *et al.* (1996), which had a residence time of 1 to 3 seconds, by conducting experiments with a shorter residence time. Furthermore, in the present study the influence of the ratio between NO and NO<sub>2</sub> was investigated since it may affect the mechanism of sensitization. The experimental data were interpreted in terms of a detailed chemical kinetics model and practical implications were outlined.

## EXPERIMENTAL

The experimental setup used for the study has been reported in detail previously (Hulgaard and Dam-Johansen, 1993; Kristensen, 1995; Glarborg *et al.*, 1995; Kristensen *et al.*, 1996), so only a brief description will be given here. In **Figure 1** a schematic view of the reactor is shown. This reactor is designed to obtain insignificant axial dispersion. Previous calculations have shown that an approximation of the reactor dynamics with a plug flow reactor is valid (Glarborg *et al.*, 1994; Kristensen, 1995). The reactor volume was 11 ml, and reactants were led to the reactor through one main and three secondary inlets. The main inlet was used for nitrogen and NO, while the secondary inlets were used for O<sub>2</sub>, NO<sub>2</sub>, CH<sub>4</sub> and in some experiments additional NO. The reactor outlet was cooled with pressurized air to ensure a well-defined reaction volume.

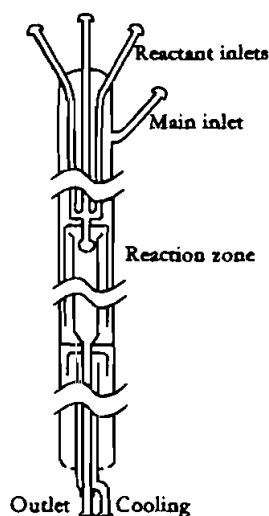


FIGURE 1 A schematic view of the quartz flow reactor design

The reactors were placed in an oven, which was designed to ensure a uniform temperature profile of the reaction zone (within  $\pm 7\text{K}$ ). The reactor temperature was monitored ( $\pm 2\text{K}$ ) using a thermo-couple mounted within the reaction zone.

Each experimental series consisted of 17 or 20 experimental points. Up to three experimental series were covered in one experiment. The reactor was set to a fixed temperature, and computer controlled valves ensured the desired combination of reagents through the reactor. A steady state was allowed to settle, before the next reagent mixture was led to the reactor, or the temperature was increased by  $25\text{K}$  to the next temperature level. In the latter case extra time was allowed for temperature to settle. Each experimental point therefore corresponds to the steady state conditions of an isothermal plug flow reactor.

The gases used in the experiments were all high purity gases, in certified concentrations (uncertainty  $\pm 2\%$ ). Inspection of FTIR spectra revealed no contamination (i.e. less than  $5\text{ppm}$ ) of the methane gas by higher hydro-carbons. The nitric oxide gas may have small (less than  $1\%$ ) impurities of  $\text{NO}_2$  and vice versa for the  $\text{NO}_2$  gas. The diluted gases were mixed at room temperatures with flow rates resulting in the desired concentrations. Since the mass flow was constant during a series, all reported residence times ( $\tau$ ) are dependent on the temperature ( $T$ ).

Analysis of the reaction products was made using standard analysers on reactor outlet gas, which was dried by cooling to  $20^\circ\text{C}$ . In addition to the standard analysers, we also recorded infra-red spectra of the outlet gases, by-passing the condensation unit, using a Bomem MB 100 FTIR instrument equipped with a gas cell with an optical path length of  $6.4\text{ m}$ . These spectra were recorded with a resolution of  $4\text{ cm}^{-1}$  and used for qualitative and quantitative identification of species. The quantitative analysis was based on subtraction of in-house recorded spectra for  $\text{CH}_4$ ,  $\text{C}_2\text{H}_4$ ,  $\text{C}_2\text{H}_6$ ,  $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{NO}$ , and  $\text{NO}_2$ . The qualitative (and semi quantitative) analysis was based on EPA library spectra for  $\text{CH}_3\text{OH}$ ,  $\text{CH}_2\text{O}$  and  $\text{CH}_3\text{NO}_2$  downloaded from Galactics Industries (1998). The carbon balance was typically satisfied within  $5\%$ .

## EXPERIMENTAL RESULTS

Essentially four types of experiments were conducted: experiments without  $\text{NO}_x$  (A), experiments with  $\text{NO}_2$  and without  $\text{NO}$  (B), experiments with  $\text{NO}$  and without  $\text{NO}_2$  (C), and experiments with  $\text{NO}$  as well as  $\text{NO}_2$  (D). When total  $\text{NO}_x$  levels were kept constant, experiments (and subsequent simulations) with  $\text{NO}$  and as little as  $20\text{ ppm}$   $\text{NO}_2$  showed results virtually identical to experiments with  $\text{NO}_2$  only. For this reason, we have chosen to report only the first three types of experiments. However, as the residence time plays a significant role in

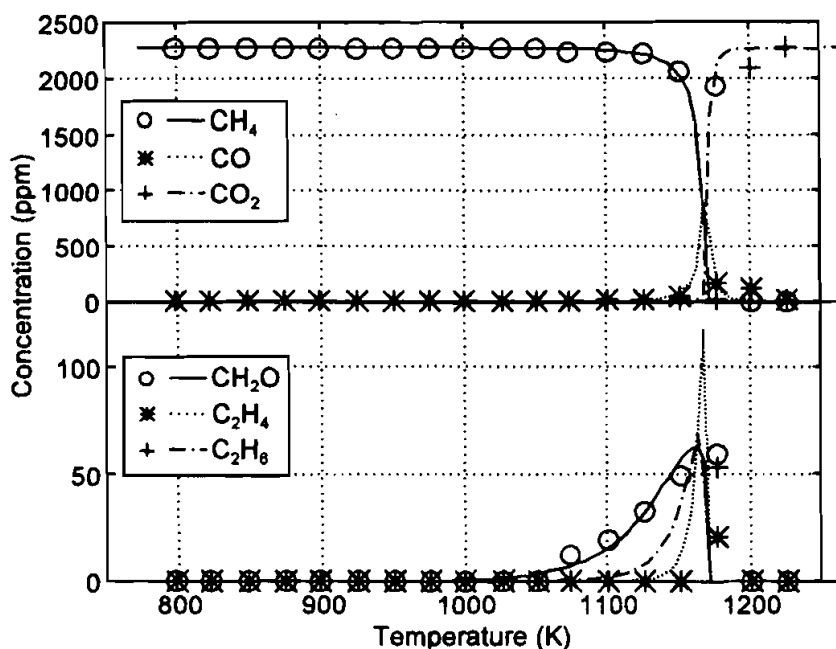


FIGURE 2 Experiment A. Methane oxidation in the absence of  $\text{NO}_x$ . Residence time was  $249.6/T$  s and other conditions as described in Table I. Symbols designate experimental observations and lines model predictions

the experiments with presence of  $\text{NO}$  only, we present two sets of results from such experiments. A summary of experimental conditions is found in Table I, and plots of experimental results are found in Figure 2 to Figure 5. A complete list of observations may be found in Appendix A.

TABLE I The experimental conditions, corresponding to the experiments reported

Experiment	Concentrations					$\tau$ (s)	Pressure (atm)
	$\text{CH}_4$ (ppm)	$\text{NO}$ (ppm)	$\text{NO}_2$ (ppm)	$\text{O}_2$ (%)	$\text{H}_2\text{O}$ (%)		
A	2276	0	0	3.69	4.00	$249.6/T$	1
B	2212	0	211	3.58	3.89	$243.6/T$	1
C	2237	205	0	3.63	3.93	$246.0/T$	1
C2	1481	186	0	2.67	6.10	$171.6/T$	1

The experimental series (A) (Figure 2) without presence of  $\text{NO}_x$  and with a residence time of 208 ms at 1200K showed little oxidation of  $\text{CH}_4$  below 1175K.

Only a narrow temperature interval up to 1200K with production of CO was observed, before complete oxidation to CO<sub>2</sub> occurred.

The experimental series (B) (**Figure 3**) with presence of 211 ppm NO<sub>2</sub> and a residence time of 202 ms at 1200K showed oxidation of CH<sub>4</sub> at temperatures as low as 950K and a wide temperature interval up to 1100K with significant levels of CO before complete oxidation to CO<sub>2</sub> was observed.

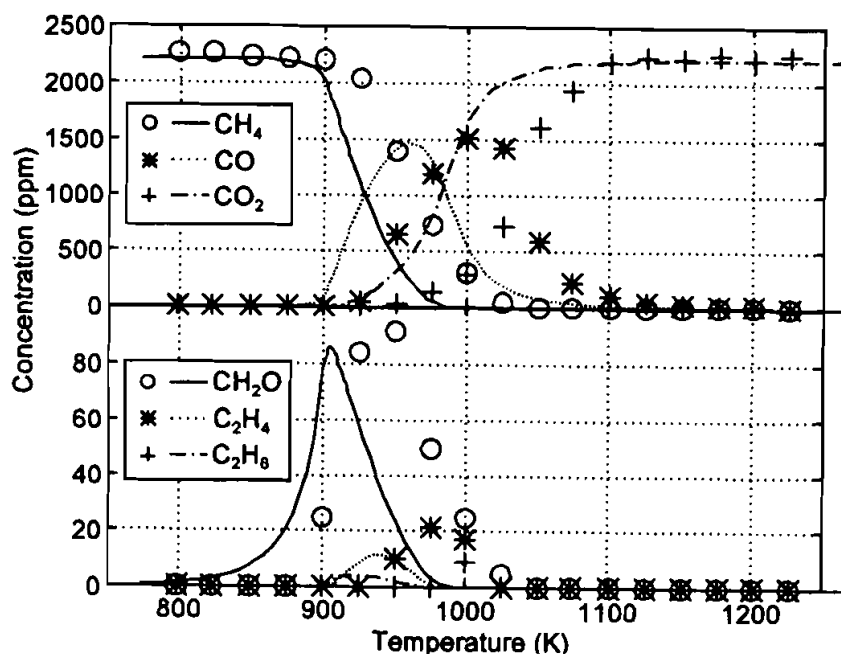


FIGURE 3 Experiment B. Methane oxidation in the presence of 211 ppm NO<sub>2</sub>. Residence time was 243.6/T s and other conditions as described in Table I. Symbols designate experimental observations and lines model predictions

The experimental series (C) (**Figure 4**) with presence of 205 ppm NO and a residence time of 205 ms at 1200K showed oxidation of CH<sub>4</sub> at 875–900K, and a wide temperature interval up to 1125K with significant production of CO before complete oxidation to CO<sub>2</sub> occurred. This is very similar to the results in series B. However, when comparing experiments at shorter residence times significant differences occur. For a residence time around 110 ms experiments with a presence of NO<sub>2</sub> (series B) showed results similar to those with a residence time of 200 ms, while experiments with presence of NO (series C2) and a residence time of 140 ms produced the results in **Figure 5**. This figure depicts an interesting phenomenon of three temperature regimes: a low temperature region (900–

1000K) with partial oxidation, an intermediate temperature regime with little reaction (1000–1150K) and a high temperature regime (>1150K) with complete oxidation. The phenomenon of a negative temperature coefficient behaviour is well known for low temperature oxidation of higher hydrocarbons and has also been reported to occur in connection with NO sensitised oxidation (Prabhu *et al.*, 1996), but to our knowledge it has not previously been observed for methane.

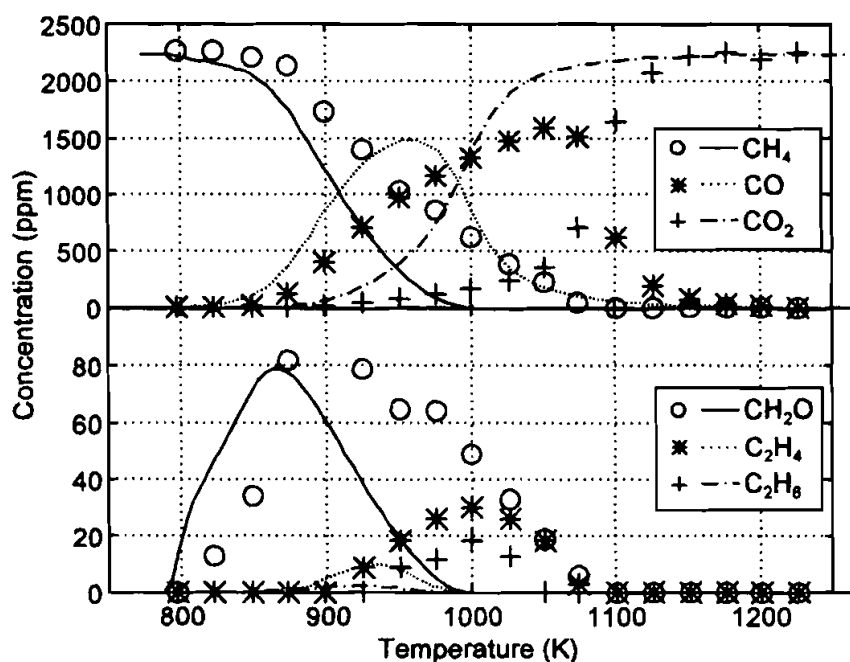


FIGURE 4 Experiment C. Methane oxidation in the presence of 205 ppm NO. Residence time was 246.0/T s and other conditions as described in Table I. Symbols designate experimental observations and lines model predictions

In all experiments analysis of FTIR spectra was made to identify intermediate products. Formation of formaldehyde, ethene and ethane at the lower temperatures was observed, while no methanol or nitromethane were detected.

## REACTION SET FOR DETAILED CHEMICAL KINETIC MODELLING

The reaction set used in the present work is based on the kinetic model of Glarborg *et al.* (1998), developed to describe NO<sub>x</sub> abatement through reburning with



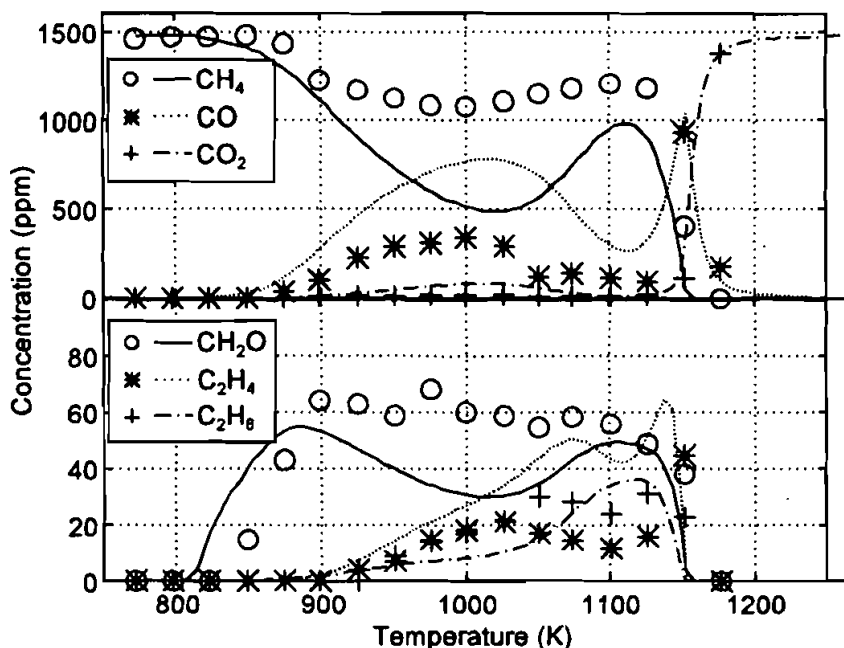


FIGURE 5 Experiment C2. Methane oxidation in the presence of 186 ppm  $\text{NO}_x$ . Residence time was 171.6/T s and other conditions as described in Table I. Symbols designate experimental observations and lines model predictions

$\text{C}_1$  and  $\text{C}_2$  hydrocarbons. Following Bromly *et al.* (1996) a number of modifications has been introduced to the reaction set to improve the description of low temperature oxidation of methane. These changes are discussed below; for a discussion of the majority of reactions the reader is referred to the paper by Glarborg *et al.* (1998). The complete reaction set is available in Appendix B.

Inspired by Bromly *et al.* (1996), the reaction set of Glarborg *et al.* (1998) was extended with reaction subsets for  $\text{CH}_3\text{O}_2$  and  $\text{CH}_3\text{NO}_2$ . The  $\text{CH}_3\text{NO}_2$  subset was taken from Glarborg *et al.* (1999) or based on analogy estimates. The  $\text{CH}_3\text{O}_2$  subset was taken mainly from the recommendations of Tsang and Hampson (1986) and Baulch *et al.* (1994). Following Bromly *et al.* (1996) we employ the reduced enthalpy of formation for  $\text{CH}_3\text{O}_2$  suggested by Slagle and Gutman (1985) instead of the higher value recommended by Burcat and McBride (1993). Finally two additional reactions between nitrogen species and carbon/hydrogen/oxygen species were added from Bromly *et al.* (1996). In this paper we will only discuss the reactions, which are of specific relevance to  $\text{NO}_x$  sensitized methane oxidation, and refer the reader to the references given above for an overall discussion of the other reactions in the reaction set.

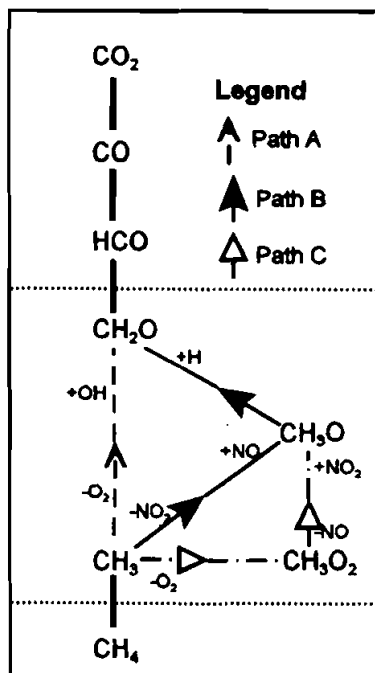
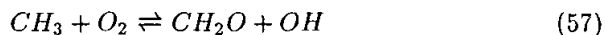


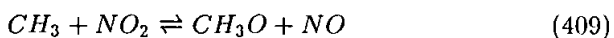
FIGURE 6 The reaction paths active in low temperature oxidation of methane. Path A dominates in the absence of  $\text{NO}_x$ . path B in the presence of  $\text{NO}_2$  and path C initiates oxidation in the presence of  $\text{NO}$  alone, but when  $\text{NO}_2$  has been produced path B dominates. — in front of a species indicate consumption and + indicate production

The key reactions for the present set of conditions are the steps consuming  $\text{CH}_3$ , as discussed below. However, before individual reaction rates are discussed the outline of the proposed reaction mechanism for  $\text{NO}_x$  sensitized methane oxidation will be presented.

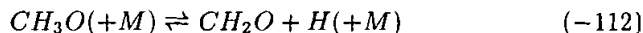
As shown in **Figure 6** the oxidation of  $\text{CH}_3$  to  $\text{CH}_2\text{O}$  may follow three paths. The direct path A, the two step path B, and the three step path C. The direct path, A, consists of reaction (57)\*:



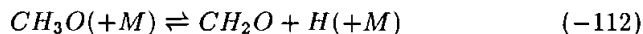
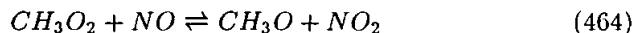
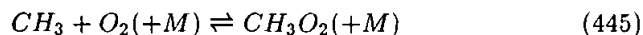
Path B ( $\text{NO}_2$  sensitized oxidation) involves reactions (409) and (-112), with regeneration of  $\text{NO}_2$  in (241).



\* The reactions will be numbered according to the listing in appendix B. A negative number indicates reference to the reverse reaction.



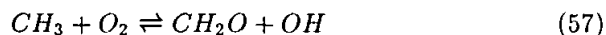
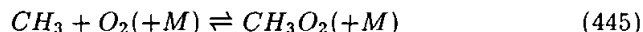
Path C (NO sensitized oxidation) consists of the steps (445), (464) and (-112),



The competition between these reaction paths, which depends both on reaction conditions and the availability and partitioning of nitrogen oxides, largely determines the oxidation behavior of methane under the reaction conditions of the present study. The key parameters, including the choice of rate constants for the critical steps, are discussed further below.

### Specific Comments to Reactions

The direct reaction path from  $\text{CH}_3$  to  $\text{CH}_2\text{O}$ , path A, consists of reaction (57). Methyl and  $\text{O}_2$  may also recombine to form  $\text{CH}_3\text{O}_2$  (445) or react through reaction (56). Reaction (445), discussed further below, is mainly important at low temperatures, where the  $\text{CH}_3\text{O}_2$  radical is sufficiently stable for reaction to compete with thermal dissociation, while reaction (56) becomes the dominant product channel of the  $\text{CH}_3 + \text{O}_2$  reaction at high temperatures.

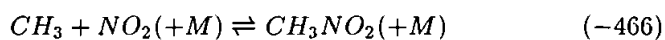
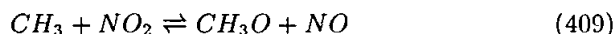


The rate constant for (56) is known within less than a factor of three at high temperatures, while reported values of the rate constant for (57) vary by more than an order of magnitude (Baulch *et al.*, 1992; Yu *et al.*, 1995). Even though most of the determinations of the rate constants for (56) and (57) are made at temperatures above 1500K, the two reactions are also important at lower temperatures. Extrapolation to 1000K of the Arrhenius expressions in the review by Baulch *et al.* (1992) leads to  $k_{56} = 1.7 \cdot 10^7 \text{ cm}^3/(\text{mol s})$  and  $k_{57} = 3.6 \cdot 10^9 \text{ cm}^3/(\text{mol s})$ , while the theoretical and experimental study by Yu *et al.* (1995) results in  $k_{56}$  and  $k_{57}$  of  $6.2 \cdot 10^6 \text{ cm}^3/(\text{mol s})$  and  $6.8 \cdot 10^7 \text{ cm}^3/(\text{mol s})$ , respectively.

The modelling predictions for the conditions of **Figure 2** (set A1) are very sensitive to the choice of rate constants for reactions (56) and (57). The fast rate constants for (56) and (57) suggested by Baulch *et al.* (1992) are inconsistent with these experiments, as well as those of Glarborg *et al.* (1998). Glarborg *et al.* preferred the rate coefficients suggested by Yu *et al.* (1995) for both reaction (56)

and (57). However, while we in the present work retain the rate constant for (56) from Yu *et al.*, we have adopted the recommendation of Bowman *et al.* (1996) for  $k_{57}$ . This value is derived from experiments performed at comparatively low temperatures, *i.e.* closer to the conditions of the present study. It is in good agreement with the recommendation of Yu *et al.* (1995) at the high temperatures of their experiments, but with a slightly lower activation energy. Thereby the chosen set of rate constants for the  $\text{CH}_3 + \text{O}_2$  reaction is consistent with the results of Yu *et al.* (1995), but with a higher product selectivity towards  $\text{CH}_2\text{O} + \text{OH}$  (57) at lower temperatures. This causes a somewhat slower oxidation rate at lower temperatures, in agreement with our experimental findings. For each  $\text{CH}_3$  radical consumed in (57), one OH radical is formed. Reaction (56) generates more radicals, since the  $\text{CH}_3\text{O}$  formed rapidly decomposes to  $\text{CH}_2\text{O}$  and H through (-112), which results in the overall production of one O and one H radical for each  $\text{CH}_3$  radical consumed.

The key step in path B ( $\text{NO}_2$  sensitized oxidation) is the reaction between  $\text{CH}_3$  and  $\text{NO}_2$ . This reaction has two significant product channels, (409) and (-466), both of which potentially are important for path B.

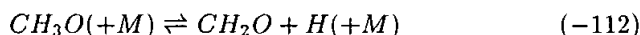
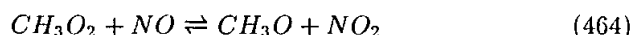
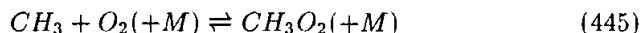


The only high temperature determination of the rate constant for (409) is the shock tube study of Glaenger and Troe (1972). The current reaction set was used in reevaluating their experiments and, as discussed by Glarborg *et al.* (1999), their reaction rate for (409) was confirmed with only a slight modification of the high temperature extrapolation.

For the  $\text{CH}_3 + \text{NO}_2(+M) \rightleftharpoons \text{CH}_3\text{NO}_2(+M)$  reaction (-466), which is in the fall-off region under the current reaction conditions, we use a center broadening factor with  $F_c = 0.183$ , following Glarborg *et al.* (1999). This results in a rate constant, which is more than a factor of five lower than the simple Lindemann expression used by Bromly *et al.* (1996).

As pointed out by Bromly *et al.* (1996) and Glarborg *et al.* (1999) the thermodynamic properties of  $\text{CH}_3\text{NO}_2$  are also subject to discussion. Since the reaction rate of (466), which is determined in the forward direction, is important mainly in the reverse direction under the present conditions, uncertainties in the entropy and enthalpy of formation for  $\text{CH}_3\text{NO}_2$  may be important under the conditions in this study. Burcat and McBride (1993) recommend values of the entropy of  $65.8 \pm 2.0$  cal/mol/s and of the enthalpy of  $-17.9 \pm 1.0$  kcal/mol, both at 298K, while Glarborg *et al.* (1999) propose  $\Delta S_f^\circ = 66.7 \pm 2.0$  cal/mol/s and  $\Delta H_f^\circ = 16.8 \pm 2.1$  kcal/mol. Simulation results with the present model using the two sets of properties were virtually identical; for this work we have chosen the values recom-

mended by Burcat and McBride (1993). Independent perturbation of  $\Delta H_f$  and  $\Delta S_f$  within the error limits may, however, shift the predicted temperature for on-set of oxidation by 25 K and a more accurate determination of the thermodynamic data for  $\text{CH}_3\text{NO}_2$  remains of relevance. Path C (NO sensitized oxidation) consists of (445), (464) and (-112).



Reaction (445) is partially equilibrated under the conditions of the present experiments, and modelling predictions are much more sensitive to the thermochemistry than to the rate constant of this reaction. The most accurate determination of the heat of formation for  $\text{CH}_3\text{O}_2$  is that of Slagle and Gutman (1985), who derive a value of  $\Delta H_f(298\text{K}) = 2.7$  kcal/mol. This value is widely used in low temperature chemistry studies (Atkinson *et al.*, 1992) and also supported by the work of Bromly *et al.* (1996). As discussed below, also the present work supports this value, which is significantly lower than the value of  $\Delta H_f(298\text{K}) = 6.7$  kcal/mol recommended by Burcat and McBride (1993).

For (464) the reaction rate is known within 30% at low temperatures (Atkinson *et al.*, 1992; Villalta *et al.*, 1995), but no measurements within the temperature range of the present study have been reported. Available results indicate that the reaction has a small negative activation energy. We have adopted the recommendation of Atkinson *et al.* (1992), which agrees fairly well with the more recent work of Villalta *et al.* (1995); extrapolations to 1000 K of the two rate constants are within a factor of two. The reaction between  $\text{CH}_4$  and  $\text{NO}_2$  (465) may constitute an important initiation step in  $\text{NO}_2$  sensitized oxidation of methane. The only available data on this reaction is from the study of Slack and Grillo (1981), who estimated the rate constant from reflected shock tube experiments on methane-oxygen ignition sensitized by  $\text{NO}_2$ , using a simplified reaction mechanism. In the present work we have reinterpreted their experiments in terms of the full reaction mechanism of App. B. Our results support their reported value of the rate constant of (465).

## SIMULATION RESULTS AND DISCUSSION

The simulation of experiments was performed with the CHEMKIN-II software package (Kee *et al.*, 1989), with the associated SENKIN code for simulation of plug flow reaction (Lutz *et al.*, 1988).

As discussed above the experiments may be treated as a series of iso-thermal plug flow reactor experiments with temperature dependent residence times. We have simulated these experiments; modeling predictions shown as lines are compared with experimental points in **Figure 2** to **Figure 4**. A qualitative correspondence between simulations and experiments is obtained, even though some deviation is observed. In general, initiation of oxidation was predicted to take place at a temperature about 25K below the temperature observed and the temperature for complete oxidation was also shifted to lower values. The over-prediction of the extent of oxidation occurs not only for the major species, but also for the C<sub>2</sub> hydrocarbons. We attribute this to over-prediction of the radical levels, rather than underestimation of the CH<sub>3</sub> radical recombination feeding into the C<sub>2</sub> species pool. If the radical pool activity is decreased (through lower formation rates or higher radical quenching rates) a less active model would be the result, and this would generally improve the modelling predictions.

The simulations correctly identify the two temperature regimes of oxidation shown in **Figure 5** and apart from over-prediction of the CO level this phenomenon is well described. Analysis of the reactions occurring shows that the reason for the two regimes is a competition between CH<sub>3</sub> oxidation pathways. At low temperatures the net (pseudo) branching path B, which corresponds to overall reaction  $\text{CH}_3 + \text{HO}_2 \rightarrow \text{CH}_2\text{O} + \text{H} + \text{OH}$ , is active. This reaction sequence converts the comparatively unreactive radicals CH<sub>3</sub> and HO<sub>2</sub> to the more reactive radicals H and OH. At intermediate temperatures the non-branching path A,  $\text{CH}_3 + \text{O}_2 \rightarrow \text{CH}_2\text{O} + \text{OH}$ , competes with path B in consuming CH<sub>3</sub> radicals, resulting in a partial inhibition of the oxidation process. As the temperature is increased further, reaction path A dominates, but chain branching in the oxidation path from CH<sub>2</sub>O to CO<sub>2</sub> secures sufficient generation of radicals for oxidation.

The prediction capability of the current reaction set was also tested against an experimental series presented by Bromly *et al.* (1996), with good results. However, for the experiments of the present work the mechanism generally predicts the oxidation process to occur at lower temperatures than observed, as it may be seen *e.g.* in **Figure 3**. In **Figure 7** the results of simulation using the reaction set proposed by Bromly *et al.* (1996) are shown. Here it is seen that the prediction of unenhanced oxidation of methane by the model of Bromly *et al.* is comparatively poor. This can be attributed mainly to their choice of rate constants for the CH<sub>3</sub> + O<sub>2</sub> reaction, as discussed above. However, NO sensitized methane oxidation is apparently predicted better by the model of Bromly *et al.* (1996) than with the current model. A sensitivity analysis of the present reaction set (**Figure 8**) did not clarify the reasons for this, but an analysis of the present reaction set and the reaction set suggested by Bromly *et al.* (1996) indicated that differences can be attributed mainly to the choice of rate constants for a few important reactions,

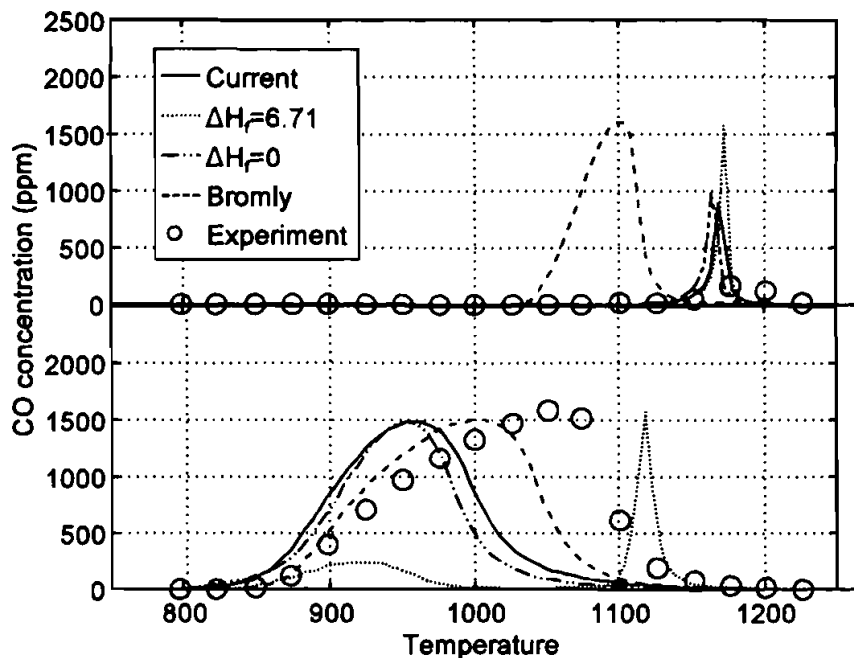
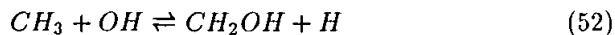
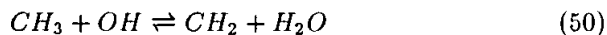
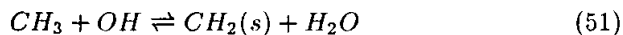
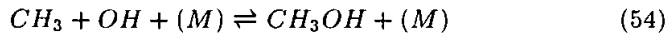


FIGURE 7 A comparison of the simulation of CO concentration from 2 experiments. In the upper plot unenhanced oxidation is shown (conditions as in Figure 2), and below NO enhanced oxidation (as in Figure 3). The reaction sets used for the simulations are "Current", the reaction set presented here; "Bromly", the reaction set proposed by Bromly *et al.* (1996); " $\Delta H_f = 6.7$ ", "Current" but with the high  $\Delta H_f(\text{CH}_3\text{O}_2) = 6.7$  kcal/mol recommended by Burcat and McBride (1993) and " $\Delta H_f = 0.0$ ", "Current" but with  $\Delta H_f(\text{CH}_3\text{O}_2) = 0.0$  kcal/mol

primarily the  $\text{CH}_3 + \text{OH}$  recombination reaction. The  $\text{CH}_3 + \text{OH}$  reaction is a multi-channel reaction that involves *a.o.* the following product channels:



In Figure 9 a comparison of the important paths for reaction between  $\text{CH}_3$  and OH according to five different sources is shown. Humpfer *et al.* (1994) assume the  $\text{CH}_3\text{OH}$  product channel to be dominating with a rate constant at 1000K of  $9 \cdot 10^{13} \text{ cm}^3/\text{mol/s}$ . However, recent experimental (Deters *et al.*, 1998) and theoretical studies (Pereira *et al.*, 1997) suggest a ten fold lower rate for (54) and favour production of  $\text{CH}_2(\text{s})$  and  $\text{H}_2\text{O}$  through (51). The high overall rate sug-



FIGURE 8 An overall sensitivity plot of the 15 most important reactions based on the time step corresponding to maximum CO concentration. Each slice of the bars corresponds to the overall sensitivity at the given conditions (A is without NO<sub>x</sub>, B with 211 ppm NO<sub>2</sub> and C with 205 ppm NO, as described in Table I). The overall sensitivity is calculated as a squared sum of normalized sensitivity of CH<sub>4</sub>, CO, CO<sub>2</sub>, NO and NO<sub>2</sub> concentrations

gested by Humpfer *et al.* (1994) is also questioned by Pereira *et al.* (1997), who attribute it to measurement error. Bromly *et al.* (1996) adopt the value of  $k_{54}$  from Humpfer *et al.* and use also a very fast rate for reaction (51), resulting in a total reaction rate between CH<sub>3</sub> and OH, which adds up to levels significantly above other experimental and theoretical reports.

The difference in performance for the two models shown in Figure 7 can mainly be attributed to the differences in rate constants for the CH<sub>3</sub> + OH reaction. This was confirmed by replacing the CH<sub>3</sub>+OH reaction rate constants in the model of Bromly *et al.* (1996) with the values from the App. B mechanism. The results are not shown here, but calculations with the modified model of Bromly *et al.* were very similar to those of our current set, *i.e.* showing the same deviations compared to experiments. Since the very fast rate for the CH<sub>3</sub> + OH reaction appears to be in error, we assume that the reason for the discrepancies seen in Figures 2 to 4 must be found somewhere else in the reaction set.

Another difference between the two mechanisms is the description of the fall-off behavior for the CH<sub>3</sub> + NO<sub>2</sub>(+M)⇌CH<sub>3</sub>NO<sub>2</sub>(+M) reaction (-466), as



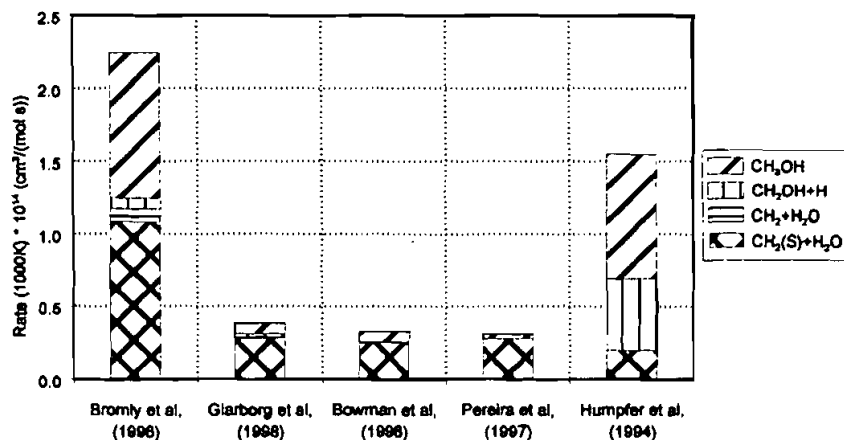


FIGURE 9 The significant product channels from the reaction between  $\text{CH}_3$  and OH according to various sources. The reaction set suggested by Bromly *et al.* (1996) combines reaction rates from various source. The reaction set of Glarborg *et al.* (1998) is identical to that used in the present study. All rates are calculated at 1000K and 1 atm

described earlier. Our use of a center broadening factor of  $F_c=0.183$  results in a rate constant, which is more than a factor of five lower than the simple Lindemann expression used by Bromly *et al.* (1996). The effect of this is a lower predicted level of  $\text{CH}_3\text{NO}_2$  production, as well as a minor reduction in the temperature for on-set of oxidation of 10 K, but otherwise the predictions of  $\text{CH}_4$ , CO and  $\text{CO}_2$  were not affected.

Figure 7 shows also the effect of varying the heat of formation of  $\text{CH}_3\text{O}_2$  within reported limits. The figure shows that high values of  $\Delta H_f$  (298K), such as that recommended by Burcat and McBride (1993) of 6.7 kcal/mol, almost remove the potential for NO enhanced methane oxidation. Consistent with the recommendation of Bromly *et al.* (1996) the results support the lower value (2.7 kcal/mol) of Slagle and Gutman (1985). In the same figure it is also demonstrated that a further reduction to  $\Delta H_f(298\text{K}) = 0$  kcal/mol does not change the prediction significantly.

The sensitivity plot in Figure 8 shows the combined sensitivity of the concentrations of  $\text{CH}_4$ , CO,  $\text{CO}_2$ , NO and  $\text{NO}_2$  towards rates of reactions by showing the sum of squared scaled sensitivities at six different sets of conditions. For each set and each species, the sensitivity coefficients were scaled through division by the span of sensitivity coefficients. The sensitivity coefficients were squared to facilitate addition of sensitivities, following Vajda *et al.* (1985). This plot largely identifies the important reactions as those shown in Figure 6, except for path C.

Path C and (445) do not show up on the sensitivity plot, because except at early reaction times the reaction is partially equilibrated. In SENKIN sensitivity coefficients are calculated by perturbing only the forward rate. If the sensitivity coefficients were calculated independently for the forward and reverse rate, they would both show up as significant. Caution must also be taken, because reaction (445) is pressure dependent. SENKIN sensitivity analysis is based on perturbing the high pressure limit for fall-off reactions, leading to misleading sensitivity coefficients in some cases. These and other short-comings of local first order sensitivity analysis, in particular the SENKIN implementation, are discussed in more detail in Bendtsen *et al.* (1999).

Since the residence time in the reactor was inversely proportional to temperature, the unexpected phenomenon of two temperature regimes of oxidation shown in **Figure 5** raised the question if the reason was a result of opposing effects of increasing temperature and decreasing residence time. However, a simulation study showed that the phenomenon remained, even though less pronounced, when a fixed residence time was chosen.

Since higher residence times would result in a more complete reaction, the over-prediction of the extent of oxidation seen in **Figure 5** raised the question of the sensitivity of the results towards variations in residence times. Simulation studies investigating this showed that the CO concentrations were only marginally sensitive towards a variation of 10 ms in the experiments with a residence time of about 140 ms (*i.e.* experimental series C2 in **Figure 5** and Appendix A). According to Kristensen (1995), 10 ms correspond to an upper limit for inlet mixing delays.

The model predicts a significant emission (up to 25 ppm) of nitromethane from the experiments. However, in the FTIR spectra there were no indications of a presence of nitromethane. This disagreement has not been clarified, but a simulation of an extraordinary slow cooling rate did not lead to a change in model predictions, thus showing that nitromethane was not expected to decompose. Therefore the predicted concentrations of nitromethane may indicate an error in the present reaction set.

Another trace emission predicted by the model is formaldehyde in levels up to 100 ppm, and these levels were generally confirmed by the FTIR spectra. As shown in **Figure 2** to **Figure 5** the predictions and experiments correspond quite well with respect to formaldehyde production. In addition to formaldehyde, also other aldehydes were predicted in the exhaust gas.

### Practical Implications of the Results

There are several important areas of application of the  $\text{NO}_x$  enhanced low temperature oxidation of methane. The dominant field is probably natural gas engines. The major aim of this study has been to uncover the processes in the exhaust of natural gas fired engines. The exhaust channel in lean burn engines has been considered to be largely unreactive chemically, but recent studies (Smith *et al.*, 1997; Kristensen *et al.*, 1999) indicate that this assumption may not be valid in general. Homogeneous conversion of NO to  $\text{NO}_2$  and even  $\text{N}_2\text{O}$  may take place (Smith *et al.*, 1997), complicating the understanding of catalytic  $\text{NO}_x$  reduction. In these systems  $\text{NO}_x$  enhanced low temperature oxidation of methane may be active in reducing the emissions of unburned hydrocarbons provided proper reaction conditions. These may be obtained either through insulation of the exhaust channel or through mounting of an expanded reactor in connection to the exhaust manifold. In addition to the desired oxidation of methane in the exhaust manifold, the  $\text{NO}_x$  enhanced low temperature oxidation of methane may produce undesired side effects such as odorous emissions, due to the partially oxygenated methane derivatives that are produced in the intermediate temperature regime. The knowledge and the modelling tools presented here may, however, help the understanding and abatement of such problems.

### CONCLUSION

The experiments presented here have confirmed the findings of Bromly *et al.* (1996) that the temperature for on-set of methane oxidation may be lowered in the presence of NO. Furthermore we have demonstrated that the presence of  $\text{NO}_2$  has a similar effect, and that the enhancement effect of NO involves a lag time, which is not seen in the presence of even small amounts of  $\text{NO}_2$ . An intermediate temperature regime with a very low extent of methane oxidation was observed when NO was present without  $\text{NO}_2$ .

The reaction set by Glarborg *et al.* (1998) has been expanded to cover the experimental range presented. The modifications of the reaction set include reaction subsets for  $\text{CH}_3\text{O}_2$  and  $\text{CH}_3\text{NO}_2$ , as well as the addition of selected reactions between hydrocarbons and NO or  $\text{NO}_2$ . It provides an acceptable prediction of the observed phenomena, but improvements of the reaction set may still be needed since the on-set of enhanced oxidation is often predicted to be 25K below the experimental observations, and CO levels are over-predicted in some cases. The prediction of nitromethane emission was not supported by experimental observations.

The mechanism of  $\text{NO}_x$  enhanced methane oxidation is based on three alternative reaction paths from  $\text{CH}_4$  to  $\text{CH}_2\text{O}$ . For enhanced oxidation to take place the presence of  $\text{NO}_2$  is needed, but if no  $\text{NO}_2$  initially is present,  $\text{NO}_2$  will be generated from  $\text{NO}$ , initializing the enhanced oxidation after a lag time.

## APPENDIX A

The experimental results: Concentrations as a function of temperature and experimental conditions. See **Table I** for experimental conditions. Unless otherwise stated results are obtained using standard analysers.

<sup>(1)</sup> Concentrations of  $\text{CH}_4$ ,  $\text{C}_2\text{H}_4$  and  $\text{C}_2\text{H}_6$  from FTIR analysis using in-house reference spectra

<sup>(2)</sup> Concentrations of  $\text{CO}_2$  from standard analyser except for values above 2000 ppm which are based on FTIR analysis using in-house reference spectra

<sup>(3)</sup> Approximate concentrations of  $\text{CH}_2\text{O}$  from FTIR analysis using external spectra.

Exp.	Temp K	Press. mbar	O <sub>2</sub> %	CH <sub>4</sub> <sup>(1)</sup> ppm	CO ppm	CO <sub>2</sub> <sup>(2)</sup> ppm	NO ppm	NO <sub>2</sub> ppm	CH <sub>2</sub> O <sup>(3)</sup> ppm	C <sub>2</sub> H <sub>4</sub> <sup>(1)</sup> ppm	C <sub>2</sub> H <sub>6</sub> <sup>(1)</sup> ppm
A	1276	1038	3.26	0	0	<sup>(2)</sup> 2258	1	0	0	0	0
A	1252	1038	3.32	0	1	<sup>(2)</sup> 2256	1	0	0	0	0
A	1227	1038	3.30	0	8	<sup>(2)</sup> 2273	1	0	0	0	0
A	1202	1038	3.33	0	122	<sup>(2)</sup> 2091	1	0	0	0	0
A	1177	1037	3.68	1933	168	27	1	0	59	21	53
A	1152	1037	3.71	2063	44	18	0	0	49	0	0
A	1126	1035	3.70	2215	17	13	1	0	32	0	0
A	1101	1035	3.73	2235	9	11	0	0	19	0	0
A	1075	1034	3.70	2235	6	9	0	0	12	0	0
A	1051	1034	3.72	2258	4	7	0	0	0	0	0
A	1027	1034	3.70	2258	3	5	0	0	0	0	0
A	1001	1034	3.73	2258	3	4	0	0	0	0	0
A	976	1035	3.70	2258	3	4	1	0	0	0	0
A	951	1035	3.73	2258	3	3	0	0	0	0	0
A	925	1035	3.70	2258	3	3	0	0	0	0	0
A	899	1034	3.73	2258	3	3	0	0	0	0	0
A	875	1035	3.70	2258	2	3	1	0	0	0	0
A	849	1036	3.73	2258	2	3	0	0	0	0	0
A	823	1037	3.71	2258	1	3	0	0	0	0	0

<i>Exp.</i>	<i>Temp K</i>	<i>Press. mbar</i>	<i>O<sub>2</sub> %</i>	<i>CH<sub>4</sub><sup>(1)</sup> ppm</i>	<i>CO ppm</i>	<i>CO<sub>2</sub><sup>(2)</sup> ppm</i>	<i>NO ppm</i>	<i>NO<sub>2</sub> ppm</i>	<i>CH<sub>2</sub>O<sup>(3)</sup> ppm</i>	<i>C<sub>2</sub>H<sub>4</sub><sup>(1)</sup> ppm</i>	<i>C<sub>2</sub>H<sub>6</sub><sup>(1)</sup> ppm</i>
A	798	1038	3.73	2258	1	2	0	0	0	0	0
B	1276	1038	3.24	0	1	(2)2256	219	0	0	0	0
B	1252	1038	3.28	0	3	(2)2256	219	1	0	0	0
B	1227	1038	3.27	0	5	(2)2256	218	2	0	0	0
B	1202	1038	3.28	0	9	(2)2207	218	2	0	0	0
B	1177	1037	3.28	0	13	(2)2245	217	3	0	0	0
B	1152	1036	3.28	0	26	(2)2227	215	5	0	0	0
B	1126	1036	3.27	0	46	(2)2229	213	6	0	0	0
B	1101	1035	3.27	0	97	(2)2188	212	6	0	0	0
B	1075	1034	3.27	0	216	1960	210	9	0	0	0
B	1051	1035	3.29	0	587	1597	208	10	0	0	0
B	1026	1035	3.32	40	1431	728	203	16	5	0	0
B	1001	1035	3.39	315	1520	328	196	21	25	17	9
B	976	1035	3.45	741	1186	149	190	25	50	21	0
B	951	1035	3.54	1397	654	44	184	26	92	10	0
B	925	1034	3.61	2046	47	2	154	55	84	0	0
B	900	1035	3.61	2207	1	2	52	137	25	0	0
B	875	1036	3.60	2224	0	2	27	158	0	0	0
B	849	1037	3.60	2233	0	2	19	159	0	0	0
B	823	1037	3.60	2258	0	2	16	162	0	0	0
B	798	1039	3.61	2258	0	2	14	164	0	0	0
C	1276	1038	3.28	0	1	(2)2234	218	0	0	0	0
C	1252	1038	3.30	0	3	(2)2256	217	1	0	0	0
C	1227	1038	3.29	0	7	(2)2249	216	2	0	0	0
C	1202	1037	3.31	0	13	(2)2185	214	3	0	0	0
C	1177	1037	3.29	0	30	(2)2253	212	4	0	0	0
C	1152	1036	3.30	0	76	(2)2216	210	5	0	0	0
C	1126	1035	3.30	0	198	(2)2067	208	8	0	0	0
C	1101	1035	3.32	0	625	1592	204	11	0	0	0
C	1075	1034	3.36	49	1512	668	197	16	6	3	0
C	1051	1034	3.40	222	1584	376	192	21	19	18	0
C	1027	1034	3.43	385	1467	251	189	24	33	26	13
C	1001	1034	3.47	613	1329	190	188	23	49	30	18
C	976	1035	3.50	847	1161	139	185	25	64	26	12
C	951	1035	3.53	1031	964	94	180	27	65	18	9

<i>Exp.</i>	<i>Temp K</i>	<i>Press. mbar</i>	<i>O<sub>2</sub> %</i>	<i>CH<sub>4</sub><sup>(1)</sup> ppm</i>	<i>CO ppm</i>	<i>CO<sub>2</sub><sup>(2)</sup> ppm</i>	<i>NO ppm</i>	<i>NO<sub>2</sub> ppm</i>	<i>CH<sub>2</sub>O<sup>(3)</sup> ppm</i>	<i>C<sub>2</sub>H<sub>4</sub><sup>(1)</sup> ppm</i>	<i>C<sub>2</sub>H<sub>6</sub><sup>(1)</sup> ppm</i>
C	926	1034	3.56	1395	713	53	170	31	79	9	0
C	899	1035	3.61	1741	392	19	161	34	105	0	0
C	874	1036	3.65	2137	114	5	170	33	82	0	0
C	849	1037	3.67	2205	15	2	187	24	34	0	0
C	823	1037	3.67	2258	2	3	200	15	0	0	0
C	797	1038	3.70	2258	0	2	214	3	0	0	0
C2	1177	1049	2.36	0	178	1394	192	2	0	0	0
C2	1152	1048	2.59	404	934	162	177	17	38	45	23
C2	1126	1049	2.72	1176	91	20	189	4	49	16	31
C2	1101	1047	2.71	1202	116	19	187	5	56	12	24
C2	1075	1048	2.71	1177	143	17	186	7	58	15	28
C2	1051	1048	2.73	1144	125	14	185	7	55	17	30
C2	1027	1047	2.70	1100	294	23	181	10	59	21	22
C2	1001	1047	2.69	1077	339	25	179	12	60	18	17
C2	976	1047	2.71	1086	306	21	175	14	68	15	14
C2	951	1046	2.70	1119	295	19	172	15	59	7	9
C2	925	1045	2.72	1169	228	14	167	17	63	4	0
C2	899	1045	2.75	1220	104	7	167	16	64	0	0
C2	875	1043	2.75	1430	36	5	174	13	43	0	0
C2	849	1041	2.75	1478	3	4	184	7	15	0	0
C2	823	1038	2.78	1469	0	3	193	0	0	0	0
C2	797	1034	2.77	1471	0	2	196	0	0	0	0
C2	772	1030	2.76	1463	0	2	196	0	0	0	0

## APPENDIX B

Reaction set and rate constants expressed as  $k = AT^\beta \exp(-E_a/RT)$ . All unit are cgs units, i.e. cal, cm<sup>3</sup>, mol and s.

	Reactions	A	$\beta$	E	Source
1	$O + OH = O_2 + H$	$2.00E + 14$	-0.40	0	
2	$O + H_2 = OH + H$	$5.00E + 04$	2.67	6290	
3	$OH + H_2 = H_2O + H$	$2.10E + 08$	1.52	3450	
4	$2OH = O + H_2O$	$4.30E + 03$	2.70	-2486	
5	$H + H + M = H_2 + M$	$1.00E + 18$	-1.00	0	
	Enhanced third-body coefficients: $H_2O = 0$				
6	$H + H + H_2O = H_2 + H_2O$	$6.00E + 19$	-1.25	0	
7	$H + O + M = OH + M$	$6.20E + 16$	-0.60	0	
	Enhanced third-body coefficients: $H_2O = 5$				
8	$H + OH + M = H_2O + M$	$1.60E + 22$	-2.00	0	
	Enhanced third-body coefficients: $H_2O = 5$				
9	$O + O + M = O_2 + M$	$1.90E + 13$	0.00	-1788	
	Enhanced third-body coefficients: $H_2O = 5$				
10	$H + O_2 + M = HO_2 + M$	$2.10E + 18$	-1.00	0	
	Enhanced third-body coefficients: $H_2O = 10; N_2 = 0$				
11	$H + O_2 + N_2 = HO_2 + N_2$	$6.70E + 19$	-1.42	0	
12	$H + HO_2 = H_2 + O_2$	$4.30E + 13$	0.00	1411	
13	$H + HO_2 = 2OH$	$1.70E + 14$	0.00	874	
14	$H + HO_2 = O + H_2O$	$3.00E + 13$	0.00	1721	
15	$O + HO_2 = O_2 + OH$	$3.30E + 13$	0.00	0	
16	$OH + HO_2 = H_2O + O_2$	$1.90E + 16$	-1.00	0	
17	$HO_2 + HO_2 = H_2O_2 + O_2$	$4.20E + 14$	0.00	11982	
	Declared duplicate reaction...				
18	$HO_2 + HO_2 = H_2O_2 + O_2$	$1.30E + 11$	0.00	-1629	
	Declared duplicate reaction...				
19	$H_2O_2 + M = OH + OH + M$	$1.30E + 17$	0.00	45500	
	Enhanced third-body coefficients: $H_2O = 5$				

	Reactions	A	$\beta$	E	Source
20	$\text{H}_2\text{O}_2 + \text{H} = \text{HO}_2 + \text{H}_2$	1.70E + 12	0.00	3755	
21	$\text{H}_2\text{O}_2 + \text{H} = \text{OH} + \text{H}_2\text{O}$	1.00E + 13	0.00	3576	
22	$\text{H}_2\text{O}_2 + \text{O} = \text{OH} + \text{HO}_2$	6.60E + 11	0.00	3974	
23	$\text{H}_2\text{O}_2 + \text{OH} = \text{H}_2\text{O} + \text{HO}_2$	7.80E + 12	0.00	1330	
	Declared duplicate reaction...				
24	$\text{H}_2\text{O}_2 + \text{OH} = \text{H}_2\text{O} + \text{HO}_2$	5.80E + 14	0.00	9560	
	Declared duplicate reaction...				
25	$\text{CO} + \text{O} + \text{M} = \text{CO}_2 + \text{M}$	6.20E + 14	0.00	3000	
	Enhanced third-body coefficients:				
	$\text{H}_2\text{O} = 5$				
26	$\text{CO} + \text{OH} = \text{CO}_2 + \text{H}$	1.50E + 07	1.30	-758	
27	$\text{CO} + \text{O}_2 = \text{CO}_2 + \text{O}$	2.50E + 12	0.00	47700	
28	$\text{HO}_2 + \text{CO} = \text{CO}_2 + \text{OH}$	5.80E + 13	0.00	22934	
29	$\text{CH}_2\text{O} + \text{M} = \text{HCO} + \text{H} + \text{M}$	3.30E + 16	0.00	81000	
	Enhanced third-body coefficients:				
	$\text{H}_2\text{O} = 5$				
30	$\text{CH}_2\text{O} + \text{H} = \text{HCO} + \text{H}_2$	1.30E + 08	1.62	2166	
31	$\text{CH}_2\text{O} + \text{O} = \text{HCO} + \text{OH}$	1.80E + 13	0.00	3080	
32	$\text{CH}_2\text{O} + \text{OH} = \text{HCO} + \text{H}_2\text{O}$	3.40E + 09	1.18	-447	
33	$\text{CH}_2\text{O} + \text{HO}_2 = \text{HCO} + \text{H}_2\text{O}_2$	3.00E + 12	0.00	13000	
34	$\text{CH}_2\text{O} + \text{O}_2 = \text{HCO} + \text{HO}_2$	6.00E + 13	0.00	40660	
35	$\text{HCO} + \text{M} = \text{H} + \text{CO} + \text{M}$	1.90E + 17	-1.00	17000	
	Enhanced third-body coefficients:				
	$\text{H}_2\text{O} = 5$				
36	$\text{HCO} + \text{H} = \text{CO} + \text{H}_2$	1.20E + 13	0.25	0	
37	$\text{HCO} + \text{O} = \text{CO} + \text{OH}$	3.00E + 13	0.00	0	
38	$\text{HCO} + \text{O} = \text{CO}_2 + \text{H}$	3.00E + 13	0.00	0	
39	$\text{HCO} + \text{OH} = \text{H}_2\text{O} + \text{CO}$	1.00E + 14	0.00	0	
40	$\text{HCO} + \text{O}_2 = \text{HO}_2 + \text{CO}$	7.60E + 12	0.00	400	
41	$\text{CH}_3 + \text{H} (+\text{M}) = \text{CH}_4 (+\text{M})$	1.30E + 16	-0.63	383	
	Low pressure limit:	1.75E + 33	-4.76	2440	
	TROE centering: 0.783 74 2941 6964				
	Enhanced third-body coefficients:				
	$\text{H}_2\text{O} = 8.57$ ; $\text{N}_2 = 1.43$				
42	$\text{CH}_4 + \text{H} = \text{CH}_3 + \text{H}_2$	1.30E + 04	3.00	8040	
43	$\text{CH}_4 + \text{O} = \text{CH}_3 + \text{OH}$	1.00E + 09	1.50	8600	



	Reactions	A	$\beta$	E	Source
44	$\text{CH}_4 + \text{OH} = \text{CH}_3 + \text{H}_2\text{O}$	1.60E + 06	2.10	2460	
45	$\text{CH}_4 + \text{HO}_2 = \text{CH}_3 + \text{H}_2\text{O}_2$	1.80E + 11	0.00	18700	
46	$\text{CH}_4 + \text{O}_2 = \text{CH}_3 + \text{HO}_2$	7.90E + 13	0.00	56000	
47	$\text{CH}_3 + \text{H} = \text{CH}_2 + \text{H}_2$	9.00E + 13	0.00	15100	
48	$\text{CH}_2(\text{s}) + \text{H}_2 = \text{CH}_3 + \text{H}$	7.20E + 13	0.00	0	
49	$\text{CH}_3 + \text{O} = \text{CH}_2\text{O} + \text{H}$	8.40E + 13	0.00	0	
50	$\text{CH}_3 + \text{OH} = \text{CH}_2 + \text{H}_2\text{O}$	7.50E + 06	2.00	5000	
51	$\text{CH}_2(\text{s}) + \text{H}_2\text{O} = \text{CH}_3 + \text{OH}$	3.00E + 15	-0.60	0	
52	$\text{CH}_2\text{OH} + \text{H} = \text{CH}_3 + \text{OH}$	1.00E + 14	0.00	0	
53	$\text{CH}_3\text{O} + \text{H} = \text{CH}_3 + \text{OH}$	1.00E + 14	0.00	0	
54	$\text{CH}_3 + \text{OH} (+\text{M}) = \text{CH}_3\text{OH} (+\text{M})$	6.30E + 13	0.00	0	
	Low pressure limit:	1.89E + 38	-6.30	3100	
	TROE centering: 0.2105 83.5 5398 8370				
	Enhanced third-body coefficients:				
	$\text{N}_2=1.43; \text{H}_2\text{O}=8.58$				
55	$\text{CH}_3 + \text{HO}_2 = \text{CH}_3\text{O} + \text{OH}$	8.00E + 12	0.00	0	
56	$\text{CH}_3 + \text{O}_2 = \text{CH}_3\text{O} + \text{O}$	2.90E + 13	0.00	30480	
57	$\text{CH}_3 + \text{O}_2 = \text{CH}_2\text{O} + \text{OH}$	3.60E + 10	0.00	8940	a
58	$\text{CH}_3 + \text{CH}_3 (+\text{M}) = \text{C}_2\text{H}_6 (+\text{M})$	2.10E + 16	-0.97	620	
	Low pressure limit:	1.26E + 50	-9.67	6220	
	TROE centering: 0.5325 151 1038 4970				
	Enhanced third-body coefficients:				
	$\text{N}_2=1.43; \text{H}_2\text{O}=8.59; \text{H}_2=2; \text{CO}=2; \text{CO}_2=3$				
59	$\text{CH}_3 + \text{CH}_2\text{O} = \text{CH}_4 + \text{HCO}$	7.80E-08	6.10	1967	
60	$\text{CH}_3 + \text{HCO} = \text{CH}_4 + \text{CO}$	1.20E + 14	0.00	0	
61	$\text{CH}_2 + \text{H} = \text{CH} + \text{H}_2$	1.00E + 18	-1.56	0	
62	$\text{CH}_2 + \text{O} = \text{CO} + \text{H} + \text{H}$	5.00E + 13	0.00	0	
63	$\text{CH}_2 + \text{O} = \text{CO} + \text{H}_2$	3.00E + 13	0.00	0	
64	$\text{CH}_2 + \text{OH} = \text{CH} + \text{H}_2\text{O}$	1.10E + 07	2.00	3000	
65	$\text{CH}_2 + \text{OH} = \text{CH}_2\text{O} + \text{H}$	2.50E + 13	0.00	0	
66	$\text{CH}_2 + \text{O}_2 = \text{CO} + \text{H}_2\text{O}$	2.20E + 22	-3.30	2867	
67	$\text{CH}_2 + \text{O}_2 = \text{CO}_2 + \text{H} + \text{H}$	3.30E + 21	-3.30	2867	
68	$\text{CH}_2 + \text{O}_2 = \text{CH}_2\text{O} + \text{O}$	3.30E + 21	-3.30	2867	
69	$\text{CH}_2 + \text{O}_2 = \text{CO}_2 + \text{H}_2$	2.60E + 21	-3.30	2867	
70	$\text{CH}_2 + \text{O}_2 = \text{CO} + \text{OH} + \text{H}$	1.60E + 21	-3.30	2867	
71	$\text{CH}_2 + \text{CO}_2 = \text{CH}_2\text{O} + \text{CO}$	1.10E + 11	0.00	1000	

	Reactions	A	$\beta$	E	Source
72	$\text{CH}_2 + \text{CH}_4 = \text{CH}_3 + \text{CH}_3$	$4.30\text{E} + 12$	0.00	10030	
73	$\text{CH}_2 + \text{CH}_3 = \text{C}_2\text{H}_4 + \text{H}$	$4.20\text{E} + 13$	0.00	0	
74	$\text{CH}_2 + \text{CH}_2 = \text{C}_2\text{H}_2 + \text{H} + \text{H}$	$4.00\text{E} + 13$	0.00	0	
75	$\text{CH}_2 + \text{HCCO} = \text{C}_2\text{H}_3 + \text{CO}$	$3.00\text{E} + 13$	0.00	0	
76	$\text{CH}_2(\text{s}) + \text{M} = \text{CH}_2 + \text{M}$	$1.00\text{E} + 13$	0.00	0	
	Enhanced third-body coefficients: H=0; H <sub>2</sub> O=0; N <sub>2</sub> =0; Ar=0				
77	$\text{CH}_2(\text{s}) + \text{N}_2 = \text{CH}_2 + \text{N}_2$	$1.30\text{E} + 13$	0.00	430	
78	$\text{CH}_2(\text{s}) + \text{Ar} = \text{CH}_2 + \text{Ar}$	$1.50\text{E} + 13$	0.00	884	
79	$\text{CH}_2(\text{s}) + \text{H} = \text{CH}_2 + \text{H}$	$2.00\text{E} + 14$	0.00	0	
80	$\text{CH}_2(\text{s}) + \text{H}_2\text{O} = \text{CH}_2 + \text{H}_2\text{O}$	$3.00\text{E} + 13$	0.00	0	
81	$\text{CH}_2(\text{s}) + \text{H} = \text{CH} + \text{H}_2$	$3.00\text{E} + 13$	0.00	0	
82	$\text{CH}_2(\text{s}) + \text{O} = \text{CO} + \text{H} + \text{H}$	$3.00\text{E} + 13$	0.00	0	
83	$\text{CH}_2(\text{s}) + \text{OH} = \text{CH}_2\text{O} + \text{H}$	$3.00\text{E} + 13$	0.00	0	
84	$\text{CH}_2(\text{s}) + \text{O}_2 = \text{CO} + \text{OH} + \text{H}$	$7.00\text{E} + 13$	0.00	0	
85	$\text{CH}_2(\text{s}) + \text{CO}_2 = \text{CH}_2\text{O} + \text{CO}$	$3.00\text{E} + 12$	0.00	0	
86	$\text{CH}_2(\text{s}) + \text{CH}_4 = \text{CH}_3 + \text{CH}_3$	$4.30\text{E} + 13$	0.00	0	
87	$\text{CH}_2(\text{s}) + \text{CH}_3 = \text{C}_2\text{H}_4 + \text{H}$	$2.00\text{E} + 13$	0.00	0	
88	$\text{CH}_2(\text{s}) + \text{CH}_2\text{CO} = \text{C}_2\text{H}_4 + \text{CO}$	$1.60\text{E} + 14$	0.00	0	
89	$\text{CH}_2(\text{s}) + \text{C}_2\text{H}_6 = \text{CH}_3 + \text{C}_2\text{H}_5$	$1.20\text{E} + 14$	0.00	0	
90	$\text{CH} + \text{H} = \text{C} + \text{H}_2$	$1.50\text{E} + 14$	0.00	0	
91	$\text{CH} + \text{O} = \text{CO} + \text{H}$	$5.70\text{E} + 13$	0.00	0	
92	$\text{CH} + \text{OH} = \text{HCO} + \text{H}$	$3.00\text{E} + 13$	0.00	0	
93	$\text{CH} + \text{OH} = \text{C} + \text{H}_2\text{O}$	$4.00\text{E} + 07$	2.00	3000	
94	$\text{CH} + \text{O}_2 = \text{HCO} + \text{O}$	$3.30\text{E} + 13$	0.00	0	
95	$\text{CH} + \text{H}_2\text{O} = \text{CH}_2\text{O} + \text{H}$	$5.70\text{E} + 12$	0.00	-751	
96	$\text{CH} + \text{CO}_2 = \text{HCO} + \text{CO}$	$3.40\text{E} + 12$	0.00	690	
97	$\text{CH} + \text{CH}_4 = \text{C}_2\text{H}_4 + \text{H}$	$6.00\text{E} + 13$	0.00	0	
98	$\text{CH} + \text{CH}_3 = \text{C}_2\text{H}_3 + \text{H}$	$3.00\text{E} + 13$	0.00	0	
99	$\text{CH} + \text{CH}_2 = \text{C}_2\text{H}_2 + \text{H}$	$4.00\text{E} + 13$	0.00	0	
100	$\text{CH} + \text{CH}_2\text{O} = \text{CH}_2\text{CO} + \text{H}$	$9.50\text{E} + 13$	0.00	-515	
101	$\text{CH} + \text{HCCO} = \text{C}_2\text{H}_2 + \text{CO}$	$5.00\text{E} + 13$	0.00	0	
102	$\text{C} + \text{OH} = \text{CO} + \text{H}$	$5.00\text{E} + 13$	0.00	0	
103	$\text{C} + \text{O}_2 = \text{CO} + \text{O}$	$2.00\text{E} + 13$	0.00	0	
104	$\text{C} + \text{CH}_3 = \text{C}_2\text{H}_2 + \text{H}$	$5.00\text{E} + 13$	0.00	0	
105	$\text{C} + \text{CH}_2 = \text{C}_2\text{H} + \text{H}$	$5.00\text{E} + 13$	0.00	0	

	Reactions	A	$\beta$	E	Source
106	$\text{CH}_3\text{OH} + \text{H} = \text{CH}_2\text{OH} + \text{H}_2$	1.70E + 07	2.10	4868	
107	$\text{CH}_3\text{OH} + \text{H} = \text{CH}_3\text{O} + \text{H}_2$	4.20E + 06	2.10	4868	
108	$\text{CH}_3\text{OH} + \text{O} = \text{CH}_2\text{OH} + \text{OH}$	3.90E + 05	2.50	3080	
109	$\text{CH}_3\text{OH} + \text{OH} = \text{CH}_2\text{OH} + \text{H}_2\text{O}$	7.10E + 06	1.80	-600	
110	$\text{CH}_3\text{OH} + \text{OH} = \text{CH}_3\text{O} + \text{H}_2\text{O}$	1.00E + 06	2.10	500	
111	$\text{CH}_3\text{OH} + \text{HO}_2 = \text{CH}_2\text{OH} + \text{H}_2\text{O}_2$	3.00E + 12	0.00	12578	
112	$\text{CH}_2\text{O} + \text{H} (+\text{M}) = \text{CH}_3\text{O} (+\text{M})$	5.40E + 11	0.45	2600	
	Low pressure limit:	1.54E + 30	4.80	5560	
	TROE centering: 0.758 94 1555 4200				
	Enhanced third-body coefficients:				
	$\text{N}_2=1.43; \text{H}_2\text{O}=8.58$				
113	$\text{CH}_3\text{O} + \text{H} = \text{CH}_2\text{O} + \text{H}_2$	2.00E + 13	0.00	0	
114	$\text{CH}_3\text{O} + \text{O} = \text{CH}_2\text{O} + \text{OH}$	1.00E + 13	0.00	0	
115	$\text{CH}_3\text{O} + \text{OH} = \text{CH}_2\text{O} + \text{H}_2\text{O}$	1.00E + 13	0.00	0	
116	$\text{CH}_3\text{O} + \text{O}_2 = \text{CH}_2\text{O} + \text{HO}_2$	6.30E + 10	0.00	2600	
117	$\text{H} + \text{CH}_2\text{O} (+\text{M}) = \text{CH}_2\text{OH} (+\text{M})$	5.40E + 11	0.45	3600	
	Low pressure limit:	9.10E + 31	-4.82	6530	
	TROE centering: 0.7187 103 1291 4160				
	Enhanced third-body coefficients:				
	$\text{N}_2=1.43; \text{H}_2\text{O}=8.58; \text{CO}=2; \text{CO}_2=3; \text{H}_2=2$				
118	$\text{CH}_2\text{OH} + \text{H} = \text{CH}_2\text{O} + \text{H}_2$	4.80E + 13	0.00	0	
119	$\text{CH}_2\text{OH} + \text{O} = \text{CH}_2\text{O} + \text{OH}$	6.50E + 13	0.00	-700	
120	$\text{CH}_2\text{OH} + \text{OH} = \text{CH}_2\text{O} + \text{H}_2\text{O}$	1.00E + 13	0.00	0	
121	$\text{CH}_2\text{OH} + \text{O}_2 = \text{CH}_2\text{O} + \text{HO}_2$	1.60E + 15	-1.00	0	
	Declared duplicate reaction...				
122	$\text{CH}_2\text{OH} + \text{O}_2 = \text{CH}_2\text{O} + \text{HO}_2$	7.20E + 13	0.00	3577	
	Declared duplicate reaction...				
123	$\text{C}_2\text{H}_6 + \text{H} = \text{C}_2\text{H}_5 + \text{H}_2$	5.40E + 02	3.50	5210	
124	$\text{C}_2\text{H}_6 + \text{O} = \text{C}_2\text{H}_5 + \text{OH}$	3.00E + 07	2.00	5115	
125	$\text{C}_2\text{H}_6 + \text{OH} = \text{C}_2\text{H}_5 + \text{H}_2\text{O}$	7.20E + 06	2.00	864	
126	$\text{C}_2\text{H}_6 + \text{HO}_2 = \text{C}_2\text{H}_5 + \text{H}_2\text{O}_2$	1.30E + 13	0.00	20460	
127	$\text{C}_2\text{H}_6 + \text{O}_2 = \text{C}_2\text{H}_5 + \text{HO}_2$	5.00E + 13	0.00	55000	
128	$\text{C}_2\text{H}_6 + \text{CH}_3 = \text{C}_2\text{H}_5 + \text{CH}_4$	5.50E-01	4.00	8300	
129	$\text{C}_2\text{H}_4 + \text{H} (+\text{M}) = \text{C}_2\text{H}_5 (+\text{M})$	1.10E + 12	0.45	1822	
	Low pressure limit:	1.11E + 34	-5.00	4448	
	TROE centering: 0.5 95 95 200				

	Reactions	A	$\beta$	E	Source
	Enhanced third-body coefficients:				
	H <sub>2</sub> O=5				
130	C <sub>2</sub> H <sub>5</sub> +H(+M)=C <sub>2</sub> H <sub>6</sub> (+M)	5.20E + 17	-0.99	1580	
	Low pressure limit:	2.00E + 41	-7.08	6685	
	TROE centering: 0.8422 125 2219 6882				
	Enhanced third-body coefficients:				
	N <sub>2</sub> =1; H <sub>2</sub> O=6; Ar=0.7				
131	C <sub>2</sub> H <sub>5</sub> +H=CH <sub>3</sub> +CH <sub>3</sub>	4.90E + 12	0.35	0	
132	C <sub>2</sub> H <sub>5</sub> +O=CH <sub>3</sub> +CH <sub>2</sub> O	4.20E + 13	0.00	0	
133	C <sub>2</sub> H <sub>5</sub> +O=CH <sub>3</sub> HCO+H	5.30E + 13	0.00	0	
134	C <sub>2</sub> H <sub>5</sub> +O=C <sub>2</sub> H <sub>4</sub> +OH	3.00E + 13	0.00	0	
135	C <sub>2</sub> H <sub>5</sub> +OH=C <sub>2</sub> H <sub>4</sub> +H <sub>2</sub> O	2.40E + 13	0.00	0	
136	C <sub>2</sub> H <sub>5</sub> +O <sub>2</sub> =C <sub>2</sub> H <sub>4</sub> +HO <sub>2</sub>	1.00E + 10	0.00	-2190	
137	C <sub>2</sub> H <sub>5</sub> +CH <sub>2</sub> O=C <sub>2</sub> H <sub>6</sub> +HCO	5.50E + 03	2.81	5860	
138	C <sub>2</sub> H <sub>5</sub> +HCO=C <sub>2</sub> H <sub>6</sub> +CO	1.20E + 14	0.00	0	
139	C <sub>2</sub> H <sub>5</sub> +CH <sub>3</sub> =C <sub>2</sub> H <sub>4</sub> +CH <sub>4</sub>	1.10E + 12	0.00	0	
140	C <sub>2</sub> H <sub>5</sub> +C <sub>2</sub> H <sub>5</sub> =C <sub>2</sub> H <sub>6</sub> +C <sub>2</sub> H <sub>4</sub>	1.50E + 12	0.00	0	
141	C <sub>2</sub> H <sub>3</sub> +H(+M)=C <sub>2</sub> H <sub>4</sub> (+M)	6.10E + 12	0.27	280	
	Low pressure limit:	9.80E + 29	-3.86	3320	
	TROE centering: 0.782 207.5 2663 6095				
	Enhanced third-body coefficients:				
	H <sub>2</sub> =2.85; CO=2.1; CO <sub>2</sub> =2.85; H <sub>2</sub> O=7.14;				
	CH <sub>4</sub> =2.85				
142	C <sub>2</sub> H <sub>4</sub> +M=C <sub>2</sub> H <sub>2</sub> +H <sub>2</sub> +M	3.50E + 16	0.00	71500	
	Enhanced third-body coefficients:				
	N <sub>2</sub> =1.5; H <sub>2</sub> O=10				
143	C <sub>2</sub> H <sub>4</sub> +H=C <sub>2</sub> H <sub>3</sub> +H <sub>2</sub>	5.40E + 14	0.00	14900	
144	C <sub>2</sub> H <sub>4</sub> +O=CH <sub>2</sub> HCO+H	4.70E + 06	1.88	180	
145	C <sub>2</sub> H <sub>4</sub> +O=CH <sub>3</sub> +HCO	8.10E + 06	1.88	180	
146	C <sub>2</sub> H <sub>4</sub> +O=CH <sub>2</sub> CO+H <sub>2</sub>	6.80E + 08	1.88	180	
147	C <sub>2</sub> H <sub>4</sub> +OH=C <sub>2</sub> H <sub>3</sub> +H <sub>2</sub> O	2.00E + 13	0.00	5940	
148	C <sub>2</sub> H <sub>4</sub> +HO <sub>2</sub> =CH <sub>3</sub> HCO+OH	2.20E + 12	0.00	17200	
149	C <sub>2</sub> H <sub>4</sub> +CH <sub>2</sub> HCO+OH	2.00E + 08	1.50	39000	
150	C <sub>2</sub> H <sub>4</sub> +CH <sub>3</sub> =C <sub>2</sub> H <sub>3</sub> +CH <sub>4</sub>	5.00E + 11	0.00	15000	
151	H+C <sub>2</sub> H <sub>2</sub> (+M)=C <sub>2</sub> H <sub>3</sub> (+M)	3.10E + 11	0.58	2590	
	Low pressure limit:	2.25E + 40	-7.27	6577	

	Reactions	A	$\beta$	E	Source
	TROE centering: 0.5 675 675				
	Enhanced third-body coefficients:				
	H <sub>2</sub> =2; CO=2; CO <sub>2</sub> =3; H <sub>2</sub> O=5				
152	C <sub>2</sub> H <sub>3</sub> +H=C <sub>2</sub> H <sub>2</sub> +H <sub>2</sub>	4.00E + 13	0.00	0	
153	C <sub>2</sub> H <sub>3</sub> +O=CH <sub>2</sub> CO+H	3.00E + 13	0.00	0	
154	C <sub>2</sub> H <sub>3</sub> +OH=C <sub>2</sub> H <sub>2</sub> +H <sub>2</sub> O	2.00E + 13	0.00	0	
155	C <sub>2</sub> H <sub>3</sub> +O <sub>2</sub> =CH <sub>2</sub> O+HCO	1.10E + 23	-3.29	3890	
156	C <sub>2</sub> H <sub>3</sub> +O <sub>2</sub> =CH <sub>2</sub> HCO+O	2.50E + 15	-0.78	3135	
157	C <sub>2</sub> H <sub>3</sub> +O <sub>2</sub> =C <sub>2</sub> H <sub>2</sub> +HO <sub>2</sub>	5.20E + 15	-1.26	3310	
158	C <sub>2</sub> H <sub>3</sub> +CH <sub>2</sub> O=C <sub>2</sub> H <sub>4</sub> +HCO	5.40E + 03	2.81	5860	
159	C <sub>2</sub> H <sub>3</sub> +HCO=C <sub>2</sub> H <sub>4</sub> +CO	9.00E + 13	0.00	0	
160	C <sub>2</sub> H <sub>3</sub> +CH <sub>3</sub> =C <sub>2</sub> H <sub>2</sub> +CH <sub>4</sub>	2.10E + 13	0.00	0	
161	C <sub>2</sub> H <sub>3</sub> +C <sub>2</sub> H <sub>3</sub> =C <sub>2</sub> H <sub>4</sub> +C <sub>2</sub> H <sub>2</sub>	1.50E + 13	0.00	0	
162	C <sub>2</sub> H <sub>2</sub> +M=C <sub>2</sub> H+H+M	9.10E + 30	-3.70	127138	
	Enhanced third-body coefficients:				
	H <sub>2</sub> =2 CO=2; CO <sub>2</sub> =3; H <sub>2</sub> O=5				
163	H <sub>2</sub> +C <sub>2</sub> H=C <sub>2</sub> H <sub>2</sub> +H	4.10E + 05	2.39	864	
164	C <sub>2</sub> H <sub>2</sub> +O=CH <sub>2</sub> +CO	6.10E + 06	2.00	1900	
165	C <sub>2</sub> H <sub>2</sub> =HCCO+H	1.40E + 07	2.00	1900	
166	C <sub>2</sub> H <sub>2</sub> +O=C <sub>2</sub> H+OH	3.20E + 15	-0.60	15000	
167	OH+C <sub>2</sub> H <sub>2</sub> =C <sub>2</sub> H+H <sub>2</sub> O	3.40E + 07	2.00	14000	
168	OH+C <sub>2</sub> H <sub>2</sub> =HCCOH+H	5.00E + 05	2.30	13500	
169	OH+C <sub>2</sub> H <sub>2</sub> =CH <sub>2</sub> CO+H	2.20E-04	4.50	-1000	
170	OH+C <sub>2</sub> H <sub>2</sub> =CH <sub>3</sub> +CO	4.80E-04	4.00	-2000	
171	OH+C <sub>2</sub> H <sub>2</sub> (+M)=C <sub>2</sub> H <sub>2</sub> OH(+M)	1.50E + 08	1.70	1000	
	Low pressure limit:	1.81E + 23	-2.00	0	
	Enhanced third-body coefficients:				
	H <sub>2</sub> =2; CO=2; CO <sub>2</sub> =3; H <sub>2</sub> O=5				
172	HO <sub>2</sub> +C <sub>2</sub> H <sub>2</sub> =CH <sub>2</sub> HCO+O	1.00E + 12	0.00	1000	
173	HO <sub>2</sub> +C <sub>2</sub> H <sub>2</sub> =CH <sub>2</sub> O+HCO	1.00E + 12	0.00	10000	
174	C <sub>2</sub> H <sub>2</sub> +O <sub>2</sub> =HCO+HCO	2.00E + 08	1.50	30100	
175	C <sub>2</sub> +H <sub>2</sub> =C <sub>2</sub> H+H	4.00E + 05	2.40	1000	
176	C <sub>2</sub> H+O=CH+CO	5.00E + 13	0.00	0	
177	C <sub>2</sub> H+OH=HCCO+H	2.00E + 13	0.00	0	
178	C <sub>2</sub> H+OH=C <sub>2</sub> +H <sub>2</sub> O	4.00E + 07	2.00	8000	
179	C <sub>2</sub> H+O <sub>2</sub> =CO+CO+H	2.50E + 13	0.00	0	

	Reactions	A	$\beta$	E	Source
180	$C_2H+CH_4=CH_3+C_2H_2$	$7.20E+12$	0.00	976	
181	$C_2+OH=C_2O+H$	$5.00E+13$	0.00	0	
182	$C_2+O_2=CO+CO$	$5.00E+13$	0.00	0	
183	$CH_3HCO=CH_3+HCO$	$7.10E+15$	0.00	81280	
184	$CH_3HCO+H=CH_3CO+H_2$	$4.10E+09$	1.16	2400	
185	$CH_3HCO+O=CH_3CO+OH$	$5.80E+12$	0.00	1800	
186	$CH_3HCO+OH=CH_3CO+H_2O$	$2.30E+10$	0.73	-1110	
187	$CH_3HCO+CH_3CO+H_2O_2$	$3.00E+12$	0.00	12000	
188	$CH_3HCO+O_2=CH_3CO+HO_2$	$3.00E+13$	0.00	39000	
189	$CH_3HCO+CH_3=CH_3CO+CH_4$	$2.00E-06$	5.60	2464	
190	$CH_2HCO=CH_3+CO$	$1.00E+13$	0.00	42000	
191	$CH_2HCO+H=CH_3+HCO$	$1.00E+14$	0.00	0	
192	$CH_2HCO+H=CH_3CO+H$	$3.00E+13$	0.00	0	
193	$CH_2HCO+O=CH_2O+HCO$	$5.00E+13$	0.00	0	
194	$CH_2HCO+OH=CH_2CO+H_2O$	$2.00E+13$	0.00	0	
195	$CH_2HCO+OH=CH_2OH+HCO$	$1.00E+13$	0.00	0	
196	$CH_2HCO+O_2=CH_2O+CO+OH$	$2.20E+11$	0.00	1500	
197	$CH_2HCO+CH_3=C_2H_5CHO$	$5.00E+13$	0.00	0	
198	$CH_2HCO+CH_2=C_2H_4+HCO$	$5.00E+13$	0.00	0	
199	$CH_2HCO+CH=C_2H_3+HCO$	$1.00E+14$	0.00	0	
200	$C_2H_5+HCO=C_2H_5CHO$	$1.80E+13$	0.00	0	
201	$C_2H_5CHO+H=C_2H_5CO+H_2$	$8.00E+13$	0.00	0	
202	$C_2H_5CHO+O=C_2H_5CO+OH$	$7.80E+12$	0.00	1730	
203	$C_2H_5CHO+OH=C_2H_5CO+H_2O$	$1.20E+13$	0.00	0	
204	$C_2H_5+CO=C_2H_5CO$	$1.50E+11$	0.00	4800	
205	$C_2H_2OH+H=CH_2HCO+H$	$5.00E+13$	0.00	0	
206	$C_2H_2OH+O=OCHCHO+H$	$5.00E+13$	0.00	0	
207	$C_2H_2OH+O_2=OCHCHO+OH$	$1.00E+12$	0.00	5000	
208	$CH_3CO(+M)=CH_3+CO(+M)$	$2.80E+13$	0.00	17100	
	Low pressure limit:	$2.10E+15$	0.00	14000	
	TROE centering: $0.5\ 1E-30\ 1E+30$				
	Enhanced third-body coefficients:				
	$H_2=2; CO=2; CO_2=3; H_2O=5$				
209	$CH_3CO+H=CH_3+HCO$	$2.10E+13$	0.00	0	
210	$CH_3CO+H=CH_2CO+H_2$	$1.20E+13$	0.00	0	
211	$CH_3CO+O=CH_3+CO_2$	$1.50E+14$	0.00	0	

	Reactions	A	$\beta$	E	Source
212	$\text{CH}_3\text{CO}+\text{O}=\text{CH}_2\text{CO}+\text{OH}$	$4.00\text{E}+13$	0.00	0	
213	$\text{CH}_3\text{CO}+\text{OH}=\text{CH}_2\text{CO}+\text{H}_2\text{O}$	$1.20\text{E}+13$	0.00	0	
214	$\text{CH}_2+\text{CO}(+\text{M})=\text{CH}_2\text{CO}(+\text{M})$	$8.10\text{E}+11$	0.50	4510	
	Low pressure limit:	$1.88\text{E}+33$	-5.11	7095	
	TROE centering: 0.5907 275 1226 5185				
	Enhanced third-body coefficients:				
	$\text{H}_2=2$ ; $\text{CO}=2$ ; $\text{CO}_2=3$ ; $\text{H}_2\text{O}=8.58$ ; $\text{N}_2=1.43$				
215	$\text{CH}_2\text{CO}+\text{H}=\text{CH}_3+\text{CO}$	$5.90\text{E}+06$	2.00	1300	
216	$\text{CH}_2\text{CO}+\text{H}=\text{HCCO}+\text{H}_2$	$3.00\text{E}+07$	2.00	10000	
217	$\text{CH}_2\text{CO}+\text{O}=\text{CO}_2+\text{CH}_2$	$1.80\text{E}+12$	0.00	1350	
218	$\text{CH}_2\text{CO}+\text{O}=\text{HCCO}+\text{OH}$	$2.00\text{E}+07$	2.00	10000	
219	$\text{CH}_2\text{CO}+\text{OH}=\text{HCCO}+\text{H}_2\text{O}$	$1.00\text{E}+07$	2.00	300	
220	$\text{CH}_2\text{CO}+\text{OH}=\text{CH}_2\text{OH}+\text{CO}$	$7.20\text{E}+12$	0.00	0	
221	$\text{CH}_2\text{CO}+\text{OH}=\text{CH}_3+\text{CO}_2$	$3.00\text{E}+12$	0.00	0	
222	$\text{HCCOH}+\text{H}=\text{HCCO}+\text{H}_2$	$3.00\text{E}+07$	2.00	1000	
223	$\text{HCCOH}+\text{OH}=\text{HCCO}+\text{H}_2\text{O}$	$1.00\text{E}+07$	2.00	1000	
224	$\text{HCCOH}+\text{O}=\text{HCCO}+\text{OH}$	$2.00\text{E}+07$	3.00	1900	
225	$\text{OCHCHO}+\text{M}=\text{HCO}+\text{HCO}+\text{M}$	$1.00\text{E}+17$	0.00	58000	
226	$\text{OCHCHO}+\text{H}=\text{CH}_2\text{O}+\text{HCO}+\text{HCO}$	$3.00\text{E}+13$	0.00	0	
227	$\text{CH}+\text{CO}(+\text{M})=\text{HCCO}(+\text{M})$	$5.00\text{E}+13$	0.00	0	
	Low pressure limit:	$1.88\text{E}+28$	-3.74	1936	
	TROE centering: 0.5757 237 1652 5069				
	Enhanced third-body coefficients:				
	$\text{N}_2=1.43$ ; $\text{H}_2\text{O}=8.58$ ; $\text{CO}=2$ ; $\text{CO}_2=3$ ; $\text{H}_2=2$				
228	$\text{H}+\text{HCCO}=\text{CH}_2(\text{s})+\text{CO}$	$1.00\text{E}+14$	0.00	0	
229	$\text{O}+\text{HCCO}=\text{H}+\text{CO}+\text{CO}$	$1.00\text{E}+14$	0.00	0	
230	$\text{HCCO}+\text{OH}=\text{C}_2\text{O}+\text{H}_2\text{O}$	$6.00\text{E}+13$	0.00	0	
231	$\text{HCCO}+\text{O}_2=\text{CO}_2+\text{CO}+\text{H}$	$1.40\text{E}+07$	1.70	1000	
232	$\text{HCCO}+\text{O}_2=\text{CO}+\text{CO}+\text{OH}$	$2.90\text{E}+07$	1.70	1000	
233	$\text{HCCO}+\text{HCCO}=\text{C}_2\text{H}_2+\text{CO}+\text{CO}$	$1.00\text{E}+13$	0.00	0	
234	$\text{C}_2\text{O}+\text{H}=\text{CH}+\text{CO}$	$1.00\text{E}+13$	0.00	0	
235	$\text{C}_2\text{O}+\text{O}=\text{CO}+\text{CO}$	$5.00\text{E}+13$	0.00	0	
236	$\text{C}_2\text{O}+\text{OH}=\text{CO}+\text{CO}+\text{H}$	$2.00\text{E}+13$	0.00	0	
237	$\text{C}_2\text{O}+\text{O}_2=\text{CO}+\text{CO}+\text{O}$	$2.00\text{E}+13$	0.00	0	
238	$\text{H}+\text{NO}+\text{M}=\text{HNO}+\text{M}$	$4.00\text{E}+20$	-1.75	0	
	Enhanced third-body coefficients:				

	Reactions	A	$\beta$	E	Source
	H <sub>2</sub> O=4.1; H <sub>2</sub> =1.25; N <sub>2</sub> = 1				
239	NO+O+M=NO <sub>2</sub> +M	7.50E + 19	-1.41	0	
	Enhanced third-body coefficients:				
	N <sub>2</sub> =1.7; O <sub>2</sub> =1.5; H <sub>2</sub> O=10				
240	OH+NO+M=HONO+M	5.10E + 23	-2.51	-68	
	Enhanced third-body coefficients:				
	H <sub>2</sub> O=5				
241	HO <sub>2</sub> +NO=NO <sub>2</sub> +OH	2.10E + 12	0.00	-479	
242	NO <sub>2</sub> +H=NO+OH	8.40E + 13	0.00	0	
243	NO <sub>2</sub> +O=NO+O <sub>2</sub>	3.90E + 12	0.00	-238	
244	NO <sub>2</sub> +O(+M)=NO <sub>3</sub> (+M)	1.30E + 13	0.00	0	
	Low pressure limit:	1.00E + 28	-4.08	2470	
	Enhanced third-body coefficients:				
	N <sub>2</sub> =1.5; O <sub>2</sub> =1.5; H <sub>2</sub> O=18.6				
245	NO <sub>2</sub> +NO <sub>2</sub> =NO+NO+O <sub>2</sub>	1.60E + 12	0.00	26123	
246	NO <sub>2</sub> +NO <sub>2</sub> =NO <sub>3</sub> +NO	9.60E + 09	0.73	20900	
247	NO <sub>3</sub> +H=NO <sub>2</sub> +OH	6.00E + 13	0.00	0	
248	NO <sub>3</sub> +O=NO <sub>2</sub> +O <sub>2</sub>	1.00E + 13	0.00	0	
249	NO <sub>3</sub> +OH=NO <sub>2</sub> +HO <sub>2</sub>	1.40E + 13	0.00	0	
250	NO <sub>3</sub> +HO <sub>2</sub> =NO <sub>2</sub> +O <sub>2</sub> +OH	1.50E + 12	0.00	0	
251	NO <sub>3</sub> +NO <sub>2</sub> =NO+NO <sub>2</sub> +O <sub>2</sub>	5.00E + 10	0.00	2940	
252	HNO+H=H <sub>2</sub> +NO	4.50E + 11	0.72	655	
253	HNO+O=NO+OH	1.00E + 13	0.00	0	
254	HNO+OH=NO+H <sub>2</sub> O	3.60E + 13	0.00	0	
255	HNO+O <sub>2</sub> =HO <sub>2</sub> +NO	1.00E + 13	0.00	25000	
256	HNO+NO <sub>2</sub> =HONO+NO	6.00E + 11	0.00	2000	
257	HNO+HNO=N <sub>2</sub> O+H <sub>2</sub> O	9.00E + 08	0.00	3100	
258	HNO+NH <sub>2</sub> =NH <sub>3</sub> +NO	3.63E + 06	1.63	-1252	
259	H <sub>2</sub> NO+M=HNO+H+M	2.50E + 15	0.00	50000	
	Enhanced third-body coefficients:				
	H <sub>2</sub> O=5; N <sub>2</sub> =2				
260	H <sub>2</sub> NO+H=HNO+H <sub>2</sub>	3.00E + 07	2.00	2000	
261	H <sub>2</sub> NO+H=NH <sub>2</sub> +OH	5.00E + 13	0.00	0	
262	H <sub>2</sub> NO+O=HNO+OH	3.00E + 07	2.00	2000	
263	H <sub>2</sub> NO+O=NH <sub>2</sub> +O <sub>2</sub>	2.00E + 14	0.00	0	
264	H <sub>2</sub> NO+OH=HNO+H <sub>2</sub> O	2.00E + 07	2.00	1000	



	Reactions	A	$\beta$	E	Source
265	$\text{H}_2\text{NO} + \text{NO} = \text{HNO} + \text{HNO}$	2.00E + 04	2.00	13000	
266	$\text{H}_2\text{NO} + \text{NO}_2 = \text{HNO} + \text{HONO}$	6.00E + 11	0.00	2000	
267	$\text{HONO} + \text{H} = \text{H}_2 + \text{NO}_2$	1.20E + 13	0.00	7352	
268	$\text{HONO} + \text{O} = \text{OH} + \text{NO}_2$	1.20E + 13	0.00	5961	
269	$\text{HONO} + \text{OH} = \text{H}_2\text{O} + \text{NO}_2$	4.00E + 12	0.00	0	
270	$\text{NH}_3 + \text{M} = \text{NH}_2 + \text{H} + \text{M}$	2.20E + 16	0.00	93470	
271	$\text{NH}_3 + \text{H} = \text{NH}_2 + \text{H}_2$	6.40E + 05	2.39	10171	
272	$\text{NH}_3 + \text{O} = \text{NH}_2 + \text{OH}$	9.40E + 06	1.94	6460	
273	$\text{NH}_3 + \text{OH} = \text{NH}_2 + \text{H}_2\text{O}$	2.00E + 06	2.04	566	
274	$\text{NH}_3 + \text{HO}_2 = \text{NH}_2 + \text{H}_2\text{O}_2$	3.00E + 11	0.00	22000	
275	$\text{NH}_2 + \text{H} = \text{NH} + \text{H}_2$	4.00E + 13	0.00	3650	
276	$\text{NH}_2 + \text{O} = \text{HNO} + \text{H}$	6.60E + 14	-0.50	0	
277	$\text{NH}_2 + \text{O} = \text{NH} + \text{OH}$	6.80E + 12	0.00	0	
278	$\text{NH}_2 + \text{OH} = \text{NH} + \text{H}_2\text{O}$	4.00E + 06	2.00	1000	
279	$\text{NH}_2 + \text{HO}_2 = \text{H}_2\text{NO} + \text{OH}$	5.00E + 13	0.00	0	
280	$\text{NH}_2 + \text{HO}_2 = \text{NH}_3 + \text{O}_2$	1.00E + 13	0.00	0	
281	$\text{NH}_2 + \text{NO} = \text{NNH} + \text{OH}$	8.90E + 12	-0.35	0	
282	$\text{NH}_2 + \text{NO} = \text{N}_2 + \text{H}_2\text{O}$	1.72E + 19	-2.29	1058	b
283	$\text{NH}_2 + \text{NO}_2 = \text{N}_2\text{O} + \text{H}_2\text{O}$	3.20E + 18	-2.20	0	
284	$\text{NH}_2 + \text{NO}_2 = \text{H}_2\text{NO} + \text{NO}$	3.50E + 12	0.00	0	
285	$\text{NH}_2 + \text{H}_2\text{NO} = \text{NH}_3 + \text{HNO}$	3.00E + 12	0.00	1000	
286	$\text{HONO} + \text{NH}_2 = \text{NO}_2 + \text{NH}_3$	7.11E + 01	3.02	-4941	
287	$\text{NH}_2 + \text{NH}_2 = \text{N}_2\text{H}_2 + \text{H}_2$	8.50E + 11	0.00	0	
288	$\text{NH}_2 + \text{NH} = \text{N}_2\text{H}_2 + \text{H}$	5.00E + 13	0.00	0	
289	$\text{NH}_2 + \text{N} = \text{N}_2 + \text{H} + \text{H}$	7.20E + 13	0.00	0	
290	$\text{NH} + \text{H} = \text{N} + \text{H}_2$	3.00E + 13	0.00	0	
291	$\text{NH} + \text{O} = \text{NO} + \text{H}$	9.20E + 13	0.00	0	
292	$\text{NH} + \text{OH} = \text{HNO} + \text{H}$	2.00E + 13	0.00	0	
293	$\text{NH} + \text{OH} = \text{N} + \text{H}_2\text{O}$	5.00E + 11	0.50	2000	
294	$\text{NH} + \text{O}_2 = \text{HNO} + \text{O}$	4.60E + 05	2.00	6500	
295	$\text{NH} + \text{O}_2 = \text{NO} + \text{OH}$	1.30E + 06	1.50	100	
296	$\text{NH} + \text{NO} = \text{N}_2\text{O} + \text{H}$	3.19E + 14	-0.46	0	
297	$\text{NH} + \text{NO} = \text{N}_2 + \text{OH}$	2.20E + 13	-0.23	0	b
298	$\text{NH} + \text{NO}_2 = \text{N}_2\text{O} + \text{OH}$	1.00E + 13	0.00	0	
299	$\text{NH} + \text{NH} = \text{N}_2 + \text{H} + \text{H}$	2.50E + 13	0.00	0	
300	$\text{NH} + \text{N} = \text{N}_2 + \text{H}$	3.00E + 13	0.00	0	

	Reactions	A	$\beta$	E	Source
301	$N+OH=NO+H$	$3.80E+13$	0.00	0	
302	$N+O_2=NO+O$	$6.40E+09$	1.00	6280	
303	$N+NO=N_2+O$	$3.30E+12$	0.30	0	
304	$N_2H_2+M=NNH+H+M$	$5.00E+16$	0.00	50000	
	Enhanced third-body coefficients: $H_2O=15; O_2=2; N_2=2; H_2=2$				
305	$N_2H_2+H=NNH+H_2$	$5.00E+13$	0.00	1000	
306	$N_2H_2+O=NH_2+NO$	$1.00E+13$	0.00	0	
307	$N_2H_2+O=NNH+OH$	$2.00E+13$	0.00	1000	
308	$N_2H_2+OH=NNH+H_2O$	$1.00E+13$	0.00	1000	
309	$N_2H_2+NO=N_2O+NH_2$	$3.00E+12$	0.00	0	
310	$N_2H_2+NH_2=NH_3+NNH$	$1.00E+13$	0.00	1000	
311	$N_2H_2+NH=NNH+NH_2$	$1.00E+13$	0.00	1000	
312	$NNH=N_2+H$	$1.00E+07$	0.00	0	
313	$NNH+H=N_2+H_2$	$1.00E+14$	0.00	0	
314	$NNH+O=N_2+OH$	$8.00E+13$	0.00	0	
315	$NNH+O=N_2O+H$	$1.00E+14$	0.00	0	
316	$NNH+O=NH+NO$	$5.00E+13$	0.00	0	
317	$NNH+OH=N_2+H_2O$	$5.00E+13$	0.00	0	
318	$NNH+O_2=N_2+HO_2$	$2.00E+14$	0.00	0	
319	$NNH+O_2=N_2+O_2+H$	$5.00E+13$	0.00	0	
320	$NNH+NO=N_2+HNO$	$5.00E+13$	0.00	0	
321	$NNH+NH_2=N_2+NH_3$	$5.00E+13$	0.00	0	
322	$NNH+NH=N_2+NH_2$	$5.00E+13$	0.00	0	
323	$N_2O+M=N_2+O+M$	$4.00E+14$	0.00	5600	
	Enhanced third-body coefficients: $N_2=1.7; O_2=1.4; H_2O=12; CO=1.5; CO_2=3$				
324	$N_2O+H=N_2+OH$	$3.30E+10$	0.00	4729	
	Declared duplicate reaction...				
325	$N_2O+H=N_2+OH$	$4.40E+14$	0.00	19254	
	Declared duplicate reaction...				
326	$N_2O+O=NO+NO$	$6.60E+13$	0.00	26630	
327	$N_2O+O=N_2+O_2$	$1.00E+14$	0.00	28000	
328	$N_2O+OH=N_2+HO_2$	$1.30E+02$	4.72	36561	
329	$N_2O+OH=HNO+NO$	$1.20E-04$	4.33	25081	
330	$N_2O+NO=NO_2+N_2$	$5.30E+05$	2.23	46281	

	Reactions	A	$\beta$	E	Source
331	CN+H <sub>2</sub> =HCN+H	3.00E + 05	2.45	2237	
332	HCN+O=NCO+H	1.40E + 04	2.64	4980	
333	HCN+O=NH+CO	3.50E + 03	2.64	4980	
334	HCN+O=CN+OH	2.70E + 09	1.58	29200	
335	HCN+OH=CN+H <sub>2</sub> O	3.90E + 06	1.83	10300	
336	HCN+OH=HOCN+H	5.90E + 04	2.40	12500	
337	HCN+OH=HNCO+H	2.00E-03	4.00	1000	
338	HCN+OH=NH <sub>2</sub> +CO	7.80E-04	4.00	4000	
339	HCN+CN=C <sub>2</sub> N <sub>2</sub> +H	1.50E + 07	1.71	1530	
340	CN+O=CO+N	7.70E + 13	0.00	0	
341	CN+OH=NCO+H	4.00E + 13	0.00	0	
342	CN+O <sub>2</sub> =NCO+O	7.50E + 12	0.00	-389	
343	CN+CO <sub>2</sub> =NCO+CO	3.70E + 06	2.16	26884	
344	CN+NO <sub>2</sub> =NCO+NO	5.30E + 15	-0.75	344	
345	CN+NO <sub>2</sub> =CO+N <sub>2</sub> O	4.90E + 14	-0.75	344	
346	CN+NO <sub>2</sub> =N <sub>2</sub> +CO <sub>2</sub>	3.70E + 14	-0.75	344	
347	CN+HNO=HCN+NO	1.80E + 13	0.00	0	
348	CN+HONO=HCN+NO <sub>2</sub>	1.20E + 13	0.00	0	
349	CN+N <sub>2</sub> O=NCN+NO	3.90E + 03	2.60	3696	
350	CN+HNCO=HCN+NCO	1.50E + 13	0.00	0	
351	CN+NCO=NCN+CO	1.80E + 13	0.00	0	
352	HNCO+M=NH+CO	1.10E + 16	0.00	86000	
353	HNCO+H=NH <sub>2</sub> +CO	2.20E + 07	1.70	3800	
354	HNCO+O=HNO+CO	1.50E + 08	1.57	44012	
355	HNCO+O=NH+CO <sub>2</sub>	9.80E + 07	1.41	8524	
356	HNCO+O=NCO+OH	2.20E + 06	2.11	11425	
357	HNCO+OH=NCO+H <sub>2</sub> O	6.40E + 05	2.00	2563	
358	HNCO+HO <sub>2</sub> =NCO+H <sub>2</sub> O <sub>2</sub>	3.00E + 11	0.00	22000	
359	HNCO+O <sub>2</sub> =HNO+CO <sub>2</sub>	1.00E + 12	0.00	35000	
360	HNCO+NH <sub>2</sub> =NH <sub>3</sub> +NCO	5.00E + 12	0.00	6200	
361	HNCO+NH=NH <sub>2</sub> +NCO	3.00E + 13	0.00	23700	
362	HOCN+H=NCO+H <sub>2</sub>	2.00E + 07	2.00	2000	
363	HOCN+O=NCO+OH	1.50E + 04	2.64	4000	
364	HOCN+OH=NCO+H <sub>2</sub> O	6.40E + 05	2.00	2563	
365	HCNO+H=HCN+OH	1.00E + 14	0.00	12000	
366	HCNO+O=HCO+NO	2.00E + 14	0.00	0	

	<i>Reactions</i>	<i>A</i>	$\beta$	<i>E</i>	<i>Source</i>
367	$\text{HCNO} + \text{OH} = \text{CH}_2\text{O} + \text{NO}$	$4.00\text{E} + 13$	0.00	0	
368	$\text{NCO} + \text{M} = \text{N} + \text{CO} + \text{M}$	$3.10\text{E} + 16$	-0.50	48000	
369	$\text{NCO} + \text{H} = \text{NH} + \text{CO}$	$5.00\text{E} + 13$	0.00	0	
370	$\text{NCO} + \text{O} = \text{NO} + \text{CO}$	$4.70\text{E} + 13$	0.00	0	
371	$\text{NCO} + \text{OH} = \text{NO} + \text{HCO}$	$5.00\text{E} + 12$	0.00	15000	
372	$\text{NCO} + \text{O}_2 = \text{NO} + \text{CO}_2$	$2.00\text{E} + 12$	0.00	20000	
373	$\text{NCO} + \text{H}_2 = \text{HNCO} + \text{H}$	$7.60\text{E} + 02$	3.00	4000	
374	$\text{NCO} + \text{HCO} = \text{HNCO} + \text{CO}$	$3.60\text{E} + 13$	0.00	0	
375	$\text{NCO} + \text{NO} = \text{N}_2\text{O} + \text{CO}$	$6.20\text{E} + 17$	-1.73	763	
376	$\text{NCO} + \text{NO} = \text{N}_2 + \text{CO}_2$	$7.80\text{E} + 17$	-1.73	763	
377	$\text{NCO} + \text{NO}_2 = \text{CO} + \text{NO} + \text{NO}$	$2.50\text{E} + 11$	0.00	-707	
378	$\text{NCO} + \text{NO}_2 = \text{CO}_2 + \text{N}_2\text{O}$	$3.00\text{E} + 12$	0.00	-707	
379	$\text{NCO} + \text{HNO} = \text{HNCO} + \text{NO}$	$1.80\text{E} + 13$	0.00	0	
380	$\text{NCO} + \text{HONO} = \text{HNCO} + \text{NO}_2$	$3.60\text{E} + 12$	0.00	0	
381	$\text{NCO} + \text{N} = \text{N}_2 + \text{CO}$	$2.00\text{E} + 13$	0.00	0	
382	$\text{NCO} + \text{NCO} = \text{N}_2 + \text{CO} + \text{CO}$	$1.80\text{E} + 13$	0.00	0	
383	$\text{C}_2\text{N}_2 + \text{O} = \text{NCO} + \text{CN}$	$4.60\text{E} + 12$	0.00	8880	
384	$\text{C}_2\text{N}_2 + \text{OH} = \text{HOCN} + \text{CN}$	$1.90\text{E} + 11$	0.00	2900	
385	$\text{NCN} + \text{O} = \text{CN} + \text{NO}$	$1.00\text{E} + 14$	0.00	0	
386	$\text{NCN} + \text{OH} = \text{HCN} + \text{NO}$	$5.00\text{E} + 13$	0.00	0	
387	$\text{NCN} + \text{H} = \text{HCN} + \text{N}$	$1.00\text{E} + 14$	0.00	0	
388	$\text{NCN} + \text{O}_2 = \text{NO} + \text{NCO}$	$1.00\text{E} + 13$	0.00	0	
389	$\text{H} + \text{CH}_3\text{CN} = \text{HCN} + \text{CH}_3$	$4.00\text{E} + 07$	2.00	2000	
390	$\text{H} + \text{CH}_3\text{CN} = \text{CH}_2\text{CN} + \text{H}_2$	$3.00\text{E} + 07$	2.00	1000	
391	$\text{O} + \text{CH}_3\text{CN} = \text{NCO} + \text{CH}_3$	$1.50\text{E} + 04$	2.64	4980	
392	$\text{OH} + \text{CH}_3\text{CN} = \text{CH}_2\text{CN} + \text{H}_2\text{O}$	$2.00\text{E} + 07$	2.00	2000	
393	$\text{CH}_2\text{CN} + \text{O} = \text{CH}_2\text{O} + \text{CN}$	$1.00\text{E} + 14$	0.00	0	
394	$\text{CN} + \text{CH}_2\text{OH} = \text{CH}_2\text{CN} + \text{OH}$	$5.00\text{E} + 13$	0.00	0	
395	$\text{H}_2\text{CN} + \text{M} = \text{HCN} + \text{H} + \text{M}$	$3.00\text{E} + 14$	0.00	22000	
396	$\text{CO} + \text{NO}_2 = \text{CO}_2 + \text{NO}$	$9.00\text{E} + 13$	0.00	33779	
397	$\text{CO} + \text{N}_2\text{O} = \text{N}_2 + \text{CO}_2$	$3.20\text{E} + 11$	0.00	20237	
398	$\text{CO}_2 + \text{N} = \text{NO} + \text{CO}$	$1.90\text{E} + 11$	0.00	3400	
399	$\text{CH}_2\text{O} + \text{NCO} = \text{HNCO} + \text{HCO}$	$6.00\text{E} + 12$	0.00	0	
400	$\text{CH}_2\text{O} + \text{NO}_2 = \text{HCO} + \text{HONO}$	$8.00\text{E} + 02$	2.77	13730	
401	$\text{HCO} + \text{NO} = \text{HNO} + \text{CO}$	$7.20\text{E} + 12$	0.00	0	
402	$\text{HCO} + \text{NO}_2 = \text{CO} + \text{HONO}$	$1.20\text{E} + 23$	-3.29	2355	

	<i>Reactions</i>	<i>A</i>	$\beta$	<i>E</i>	<i>Source</i>
403	$\text{HCO} + \text{NO}_2 = \text{H} + \text{CO}_2 + \text{NO}$	$8.40\text{E} + 15$	-0.75	1930	
404	$\text{HCO} + \text{HNO} = \text{CH}_2\text{O} + \text{NO}$	$6.00\text{E} + 11$	0.00	2000	
405	$\text{CH}_4 + \text{CN} = \text{CH}_3 + \text{HCN}$	$6.20\text{E} + 04$	2.64	-437	
406	$\text{NCO} + \text{CH}_4 = \text{CH}_3 + \text{HNCO}$	$9.80\text{E} + 12$	0.00	8120	
407	$\text{CH}_3 + \text{NO} = \text{HCN} + \text{H}_2\text{O}$	$1.50\text{E}-01$	3.52	3950	
408	$\text{CH}_3 + \text{NO} = \text{H}_2\text{CN} + \text{OH}$	$1.50\text{E}-01$	3.52	3950	
409	$\text{CH}_3 + \text{NO}_2 = \text{CH}_3\text{O} + \text{NO}$	$4.00\text{E} + 13$	-0.20	0	c
410	$\text{CH}_3 + \text{N} = \text{H}_2\text{CN} + \text{H}$	$7.10\text{E} + 13$	0.00	0	
411	$\text{CH}_3 + \text{CN} = \text{CH}_2\text{CN} + \text{H}$	$1.00\text{E} + 14$	0.00	0	
412	$\text{CH}_3 + \text{HOCN} = \text{CH}_3\text{CN} + \text{OH}$	$5.00\text{E} + 12$	0.00	2000	
413	$\text{CH}_2 + \text{NO} = \text{HCN} + \text{OH}$	$2.20\text{E} + 12$	0.00	-378	
414	$\text{CH}_2 + \text{NO} = \text{HCNO} + \text{H}$	$1.30\text{E} + 12$	0.00	-378	
415	$\text{CH}_2 + \text{NO}_2 = \text{CH}_2\text{O} + \text{NO}$	$5.90\text{E} + 13$	0.00	0	
416	$\text{CH}_2 + \text{N} = \text{HCN} + \text{H}$	$5.00\text{E} + 13$	0.00	0	
417	$\text{CH}_2 + \text{N}_2 = \text{HCN} + \text{NH}$	$1.00\text{E} + 13$	0.00	74000	
418	$\text{H}_2\text{CN} + \text{N} = \text{N}_2 + \text{CH}_2$	$2.00\text{E} + 13$	0.00	0	
419	$\text{CH}_2(\text{s}) + \text{NO} = \text{HCN} + \text{OH}$	$2.00\text{E} + 13$	0.00	0	
420	$\text{CH}_2(\text{s}) + \text{NO} = \text{CH}_2 + \text{NO}$	$1.00\text{E} + 14$	0.00	0	
421	$\text{CH}_2(\text{s}) + \text{HCN} = \text{CH}_3 + \text{CN}$	$5.00\text{E} + 13$	0.00	0	
422	$\text{CH} + \text{NO}_2 = \text{HCO} + \text{NO}$	$1.00\text{E} + 14$	0.00	0	
423	$\text{CH} + \text{NO} = \text{HCN} + \text{O}$	$4.80\text{E} + 13$	0.00	0	
424	$\text{CH} + \text{NO} = \text{HCO} + \text{N}$	$3.40\text{E} + 13$	0.00	0	
425	$\text{CH} + \text{NO} = \text{NCO} + \text{H}$	$1.90\text{E} + 13$	0.00	0	
426	$\text{CH} + \text{N} = \text{CN} + \text{H}$	$1.30\text{E} + 13$	0.00	0	
427	$\text{CH} + \text{N}_2 = \text{HCN} + \text{N}$	$3.70\text{E} + 07$	1.42	20723	
428	$\text{CH} + \text{N}_2\text{O} = \text{HCN} + \text{NO}$	$1.90\text{E} + 13$	0.00	-511	
429	$\text{C} + \text{NO} = \text{CN} + \text{O}$	$2.00\text{E} + 13$	0.00	0	
430	$\text{C} + \text{NO} = \text{CO} + \text{N}$	$2.80\text{E} + 13$	0.00	0	
431	$\text{C} + \text{N}_2 = \text{CN} + \text{N}$	$6.30\text{E} + 13$	0.00	46019	
432	$\text{C} + \text{N}_2\text{O} = \text{CN} + \text{NO}$	$5.10\text{E} + 12$	0.00	0	
433	$\text{C}_2\text{H}_6 + \text{CN} = \text{C}_2\text{H}_5 + \text{HCN}$	$1.20\text{E} + 05$	2.77	-1788	
434	$\text{C}_2\text{H}_6 + \text{NCO} = \text{C}_2\text{H}_5 + \text{HNCO}$	$1.50\text{E}-09$	6.89	-2910	
435	$\text{C}_2\text{H}_4 + \text{CN} = \text{C}_2\text{H}_3 + \text{HCN}$	$5.90\text{E} + 14$	-0.24	0	
436	$\text{C}_2\text{H}_3 + \text{NO} = \text{C}_2\text{H}_2 + \text{HNO}$	$1.00\text{E} + 12$	0.00	1000	
437	$\text{C}_2\text{H}_3 + \text{N} = \text{HCN} + \text{CH}_2$	$2.00\text{E} + 13$	0.00	0	
438	$\text{C}_2\text{H}_2 + \text{NCO} = \text{HCCO} + \text{HCN}$	$1.40\text{E} + 12$	0.00	1815	

	Reactions	A	$\beta$	E	Source
439	$C_2H+NO=CN+HCO$	$2.10E+13$	0.00	0	
440	$CH_2CO+CN=HCCO+HCN$	$2.00E+13$	0.00	0	
441	$HCCO+NO=HCNO+CO$	$7.20E+12$	0.00	0	
442	$HCCO+NO=HCN+CO_2$	$1.60E+13$	0.00	0	
443	$HCCO+NO_2=HCNO+CO_2$	$1.60E+13$	0.00	0	
444	$HCCO+N=HCN+CO$	$5.00E+13$	0.00	0	
445	$CH_3+O_2(+M)=CH_3O_2(+M)$	$7.80E+08$	1.20	0	d
	Low pressure limit:	$5.40E+25$	-3.30	0	
	Enhanced third-body coefficients:				
	$N_2=1.1; H_2O=10$				
446	$CH_3O_2+H=CH_3O+OH$	$1.00E+14$	0.00	0	e
447	$CH_3O_2+O=CH_3O+O_2$	$3.60E+13$	0.00	0	e
448	$CH_3O_2+CH_3OH+O_2$	$6.00E+13$	0.00	0	e
449	$CH_3O_2+HO_2=CH_3OOH+O_2$	$2.50E+11$	0.00	-1570	d
450	$CH_3O_2+H_2O=CH_3OOH+HO_2$	$2.40E+12$	0.00	9940	e
451	$CH_3O_2+CH_2O=CH_3OOH+HCO$	$2.00E+12$	0.00	11665	e
452	$CH_3O_2+CH_4=CH_3OOH+CH_3$	$1.80E+11$	0.00	18500	e
453	$CH_3O_2+CH_3=CH_3O+CH_3O$	$2.40E+13$	0.00	0	e
454	$CH_3O_2+CH_3O=CH_2O+CH_3OOH$	$3.00E+11$	0.00	0	e
455	$CH_3O_2+CH_2OH=CH_2O+CH_3OOH$	$1.20E+13$	0.00	0	e
456	$CH_3O_2+CH_3OH=CH_3OOH+CH_2OH$	$1.80E+12$	0.00	13700	e
457	$CH_3O_2+CH_3O_2=CH_3O+CH_3O+O_2$	$1.00E+11$	0.00	300	d
458	$CH_3O_2+CH_3O_2=CH_3OH+CH_2O+O_2$	$4.00E+09$	0.00	-2210	d
459	$CH_3OOH=CH_3O+OH$	$6.30E+14$	0.00	42300	f
460	$CH_3OOH+H=CH_3O_2+H_2$	$8.80E+10$	0.00	1860	g
461	$CH_3OOH+H=CH_3O+H_2O$	$8.20E+10$	0.00	1860	g
462	$CH_3OOH+O=CH_3O_2+OH$	$1.00E+12$	0.00	3000	h
463	$CH_3OOH+OH=CH_3O_2+H_2O$	$1.80E+12$	0.00	-378	i
464	$CH_3O_2+NO=CH_3O+NO_2$	$2.53E+12$	0.00	-358	i
465	$CH_4+NO_2=CH_3+HONO$	$1.20E+13$	0.00	30000	j
466	$CH_3NO_2(+M)=CH_3+NO_2(+M)$	$1.80E+16$	0.00	58500	c
	Low pressure limit:	$1.30E+17$	0.00	42000	
	TROE centering: $0.183 \text{ 1E-30 1E+30}$				
467	$CH_3NO_2+H=HONO+CH_3$	$3.30E+12$	0.00	3730	c
468	$CH_3NO_2+H=CH_3NO+OH$	$1.40E+12$	0.00	3730	c
469	$CH_3NO_2+H=H_2CNO_2+H_2$	$5.40E+02$	3.50	5200	c

	Reactions	A	$\beta$	E	Source
470	$\text{CH}_3\text{NO}_2 + \text{O} = \text{H}_2\text{CNO}_2 + \text{OH}$	$1.50\text{E} + 13$	0.00	5350	c
471	$\text{CH}_3\text{NO}_2 + \text{OH} = \text{H}_2\text{CNO}_2 + \text{H}_2\text{O}$	$5.00\text{E} + 05$	2.00	1000	c
472	$\text{CH}_3\text{NO}_2 + \text{OH} = \text{CH}_3\text{OH} + \text{NO}_2$	$2.00\text{E} + 10$	0.00	-1000	c
473	$\text{CH}_3\text{NO}_2 + \text{HO}_2 = \text{H}_2\text{CNO}_2 + \text{H}_2\text{O}_2$	$3.00\text{E} + 12$	0.00	23000	k
474	$\text{CH}_3\text{NO}_2 + \text{O}_2 = \text{H}_2\text{CNO}_2 + \text{HO}_2$	$2.00\text{E} + 13$	0.00	57000	k
475	$\text{CH}_3\text{NO}_2 + \text{CH}_3 = \text{CH}_4 + \text{H}_2\text{CNO}_2$	$5.50\text{E}-01$	4.00	8300	c
476	$\text{CH}_3\text{NO}_2 + \text{CH}_2(\text{s}) = \text{CH}_3 + \text{H}_2\text{CNO}_2$	$1.20\text{E} + 14$	0.00	0	c
477	$\text{CH}_3\text{NO}_2 + \text{CH}_2 = \text{CH}_3 + \text{H}_2\text{CNO}_2$	$6.50\text{E} + 12$	0.00	7900	c
478	$\text{CH}_3\text{NO}_2 + \text{CH}_3\text{O} = \text{H}_2\text{CNO}_2 + \text{CH}_3\text{OH}$	$3.00\text{E} + 11$	0.00	7000	k
479	$\text{CH}_3\text{NO}_2 + \text{NO}_2 = \text{H}_2\text{CNO}_2 + \text{HONO}$	$3.00\text{E} + 11$	0.00	32000	c
480	$\text{H}_2\text{CNO}_2 = \text{CH}_2\text{O} + \text{NO}$	$1.00\text{E} + 13$	0.00	36000	c
481	$\text{H}_2\text{CNO}_2 + \text{H} = \text{CH}_3 + \text{NO}_2$	$5.00\text{E} + 13$	0.00	0	l
482	$\text{H}_2\text{CNO}_2 + \text{O} = \text{CH}_2\text{O} + \text{NO}_2$	$5.00\text{E} + 13$	0.00	0	l
483	$\text{H}_2\text{CNO}_2 + \text{OH} = \text{CH}_2\text{OH} + \text{NO}_2$	$1.00\text{E} + 13$	0.00	0	l
484	$\text{H}_2\text{CNO}_2 + \text{OH} = \text{CH}_2\text{O} + \text{HONO}$	$1.00\text{E} + 13$	0.00	0	l

References: Where no source is provided, the reference is Glarborg *et al.* (1998). a) Bowman *et al.* (1996), b) Fitted from difference between two reactions given in Glarborg *et al.* (1998), c) Glarborg *et al.* (1999), d) Baulch *et al.* (1994), e) Tsang and Hampson (1986), f) Lightfoot *et al.* (1991), g) Slemr and Warneck (1977), h) Vaghjiani and Ravishankara (1990), i) Atkinson *et al.* (1992), j) Slack and Grillo (1981), k) Estimate from analogy with  $\text{C}_2\text{H}_6$  reactions, l) Rough estimate, m) Burcat and McBride (1993), n) Lightfoot *et al.* (1992).

#### Selected thermodynamic properties:

Species	$\Delta H_f^{298}$ (cal/mole)	$S_{298}$ (cal/mole/K)	$C_{p300}$	$C_{p400}$	$C_{p500}$	$C_{p600}$	$C_{p800}$	$C_{p1000}$	$C_{p1500}$	Source
			(cal/mole/K)							
$\text{CH}_3\text{NO}_2$	-17.86	65.73	13.72	16.94	19.69	22.02	25.66	28.21	31.77	m
$\text{CH}_3\text{O}_2$	2.70	64.20	13.11	15.63	17.79	19.63	22.52	24.56	27.4	n

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