Journal of Physical and Chemical Reference Data

Chemical Kinetic Data Base for Combustion Chemistry. Part 2. Methanol

Cite as: Journal of Physical and Chemical Reference Data **16**, 471 (1987); https://doi.org/10.1063/1.555802
Submitted: 09 October 1986 . Published Online: 15 October 2009

Wing Tsang

Chemical Kinetic Data Base for Combustion Chemistry. Part 2. Methanol

Wing Tsang

Chemical Kinetics Division, National Bureau of Standards, Gaithersburg, Maryland 20899

Received October 9, 1986; revised manuscript received March 3, 1987

This publication contains evaluated and estimated data on the kinetics of reactions involving methanol and hydroxymethyl radicals and various small inorganic and organic species which are of importance for the proper understanding of methanol combustion and pyrolysis. It is meant to be used in conjunction with the kinetic data given in an earlier publication pertaining to methane pyrolysis and combustion, but which also contains a large volume of data that are applicable to the methanol system. The temperature range covered is 300–2500 K and the density range 1×10^{16} to 1×10^{21} molecules cm^{-3}.

Key words: combustion; data base; evaluation; gas kinetics; hydroxymethyl; methanol; rate expressions.

Contents

1. Introduction

1.1. Scope

This is the second of a series of publications presenting evaluated chemical kinetic data important for the detailed understanding of the combustion of organic compounds. Previously[1], we dealt with the reactions of the most likely species present in methane combustion. We now add two new species, CH_3OH and CH_2OH, to this list and include the 41 reactions of these two compounds with the components involved in methane combustion and the reactions with each other. With the appropriate reactions in the earlier[1] data base we are now in a position to give a complete description of the chemistry of methanol combustion. We have selected methanol as the first addition to our data base because of the interest in its use as an alternative fuel. As a result more new kinetic data have been reported[2]. There have also been attempts at modeling methanol decomposition systems[3]. Finally, because methanol is the simplest of the alcohols, many of the reactions are of use in understanding and modeling the oxidation and pyrolysis of other alcohols.

Our approach has been to be as inclusive as possible. Having decided on the important species, we consider all the possible reactions of these species. Where experimental information is not available we give our best estimate. The absence of a recommended number implies that for all purposes the rate constant is sufficiently small that it can be ignored. The reaction grid containing the reactions that we have evaluated in the past and the one presented in this evaluation can be found in Fig. 1. In all cases we have given recommended values that cover the temperature range of 300–2500 K and the density range of 1×10^{16}–1×10^{21} molecules cm^{-3}.

1.2. Organization

The data are presented in the same fashion as in the earlier evaluation on methane combustion[1]. The information contained here is meant to be used in conjunction with that in our earlier publication. A more detailed presentation of what is contained in this introduction can be found there. This discussion contains the minimal information necessary for the use of the present data.

The data are presented in three sections. The first contains a summary of the recommended rate expressions, the estimated error factors, and the page where a brief discussion can be found. The second section contains additional information on the individual reactions. It includes a summary of past work and the justification for the recommendations. The third section contains relevant thermodynamic and transport property data.

Reprints available from ACS; see Reprints List at back of issue.

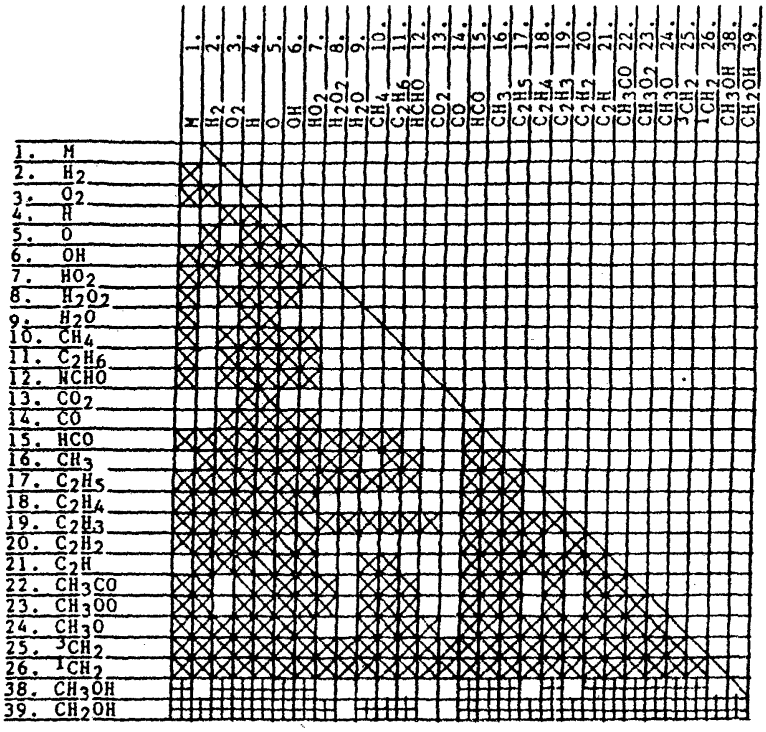

Fig. 1. Reaction grid. ×: Reactions covered in Ref. 1. +: Reactions covered in present work.

1.3. Guide to Summary Table

The summary table contains all the recommended rate expressions, the uncertainty factors and the page where a more detailed discussion can be found. For unimolecular processes or their reverse combination we give results in terms of the high pressure or low pressure limit and the departure from this limit in the form of the ratio k/k_∞ or k/k_0 (where the subscript refers to the limiting high and low pressures) for 1 atm N_2 or Ar.

1.4. Guide to Chemical Kinetic Data Tables

This section contains information on past work, our analysis of the data, rate expression recommendations, and uncertainty factors. We retain the numbering system that we use for the methane combustion system: to the twenty-five species that are labeled from 2 to 26 we now add 38 (methanol) and 39 (hydroxymethyl). The label 1 is reserved for unimolecular reactions. We are also reserving the labels 27–37 for the species of importance to NO_x formation processes. Since pairs of these numbers form a particular reaction, we now consider reactions 38 (methanol) and 39 (hydroxymethyl) with all lower numbered species and of course with themselves. These sequence numbers are at the top left hand corner of all the data tables. This is followed by a statement of the elementary reaction and, if applicable, the appropriate equilibrium constant.

In the next section is a synopsis of all previous work. It begins with a listing of the author(s) and the year of publication. In the case of a review, a note is made to this effect and in many cases this is used as a starting point for our efforts. This is followed by a synopsis of the reaction conditions, the derived rate expressions and the uncertainty limits. The latter are either given by the author or estimated by the reviewer on the basis of similar experiments. Most of the reactions are bimolecular and the units are cm^3 $molecule^{-1}$ s^{-1}. For unimolecular and termolecular reactions the units are s^{-1} and cm^6 $molecule^{-2}$ s^{-1} respectively. As an aid to the user in those cases where there are considerable experimental data we also include a plot in the Arrhenius form of the data and our recommendations.

The next section contains our recommendations and a brief discussion of our rationale. We have discussed our approach in detail in our earlier paper[1]. Here, we simply note that we have used BEBO[4] transition states to fit hydrogen abstraction data over the 300–2500 K temperature range of interest. This leads in general to a $T^2 - T^4$ temperature dependence for the preexponential factor. Unimolecular reactions and related processes are pressure and species (weak colliders) dependent as well as temperature dependent. We have applied standard RRKM[5] calculations to model the pressure and weak collider dependence. Unfortunately, the results could not be expressed in closed form. We have therefore presented the results in the form of a rate expression for either the high pressure or low pressure (strong collision) limit and two tables from which rate constants at reaction conditions can be obtained by interpolation. The choice of the appropriate rate expression was dictated by the closeness of the reaction to these limits under combustion conditions. The first table is the result of RRKM calculations on the basis of the strong collision assumption, with the collision partner being the reactant itself, and leads to values of k/k_∞ or k/k_o as a function of temperature and pressure. These values are essentially correction factors to the limiting high or low pressure rate constants. The second table gives the collision efficiency, $\beta(e)$ (on a per collision basis), as a function of step size down (energy removed per collision). The tabulated results are based on the relation of Troe[6]. At the present time there is controversy regarding the magnitude and temperature dependence of this quantity. We have thus cast it in this form so that users can employ their own step sizes. The values in both tables refer to the reactant itself as the collider. In order to convert these values to those for an arbitrary collider we follow the approach of Troe[6] and derive a correction factor, $\beta(c)$, which is based on the ratio of the collisional properties of reactant and collider. Multiplying this factor by the collision efficiency derived earlier leads to a total collision efficiency, $\beta(t)=\beta(e)\times\beta(c)$. $\beta(t)$ is then used to scale the reaction pressure in our table and thus obtain an effective pressure for determining the rate constant ratios.

We illustrate the situation by carrying out fall-off calculations for methanol decomposition in the case of a dilute methanol in argon mixture at 1500 K. As an aid to the user, the calculations are carried out to many more places than justified by the accuracy of the data. This should prevent any ambiguities. We begin by determining $\beta(c)$. This involves the calculation of a number of ratios. In the following, the numerator refers to the properties of the methanol-argon mixture, while the denominator refers to pure methanol itself.

a) Ratio of reduced masses (R); for methanol and argon this number is 17.78(methanol-argon)/16(methanol-methanol)=1.111.

b) Ratio of collision diameters (C); for a methanol argon mixture, this ratio is [3.626(methanol) + 3.542(argon)]/[3.626(methanol)×2]=0.985.

c) Ratio of collision integrals (W); where we use the approximation $W=1/(0.697 + 0.5185\times\log[kT/\epsilon$ (argon-methanol)$])^{6,7}$ and ϵ/k (argon-methanol) $=([\epsilon$ (argon)$/k][\epsilon$(methanol)$/k])^{0.5}$ where ϵ/k is the Lennard Jones well depth. Since ϵ/k is 481.8 K for methanol and 93.3 K for argon, then the ratio of the collision integrals is 0.879/1.049=0.922.

The correction factor is then, $\beta(c) = C^2W/R^{0.5}=0.849$.

For the methanol-argon mixture with a 600 cm^{-1} step size down the collision efficiency on a per collision basis at 1500 K is, $\beta(e) = 0.082$ (see 38,1). The total collision efficiency is then $\beta(t) = \beta(c)\times\beta(e) = 0.082\times0.849 = 0.07$. At 20 atmospheres or 10^{20} molecules/cm^3 this is equivalent to a density of 7×10^{18} molecules cm^{-3}. From Table A of 38,1 we then find $k/k_\infty=0.38$.

Systems for which the low pressure rate expression is given require the same procedure except that the final bimolecular rate constant is now given by the expression $\beta(t)\times k_o\times(k/k_o)$. For chemical activation processes the rate expressions can be obtained in an analogous manner. In addition to the possible pressure dependence of the total rate, the ratio of decomposition to stabilization is also of importance. Thus, in these cases we include a table giving this ratio as a function of temperature and pressure on the assumption of strong collisions. Note that the procedure for correction for weak collision effects in the chemical activation systems is an untested approximation. Fortunately, for the systems considered here, pressure effects are relatively unimportant.

In the course of carrying out the earlier evaluation[1], we found that the data for unimolecular fall-off can generally be fitted, in the context of weak collisions, by step sizes of 50–100 cm^{-1} near room temperature and 500–800 cm^{-1} under higher temperature combustion conditions (>900 K). This was also borne out in the present study for methanol decomposition with argon as the weak collider. For strong colliders the situation is less clear, but the earlier existing data[1] suggest step sizes down in the 1000–2000 cm^{-1} range. As an additional aid to the user and to eliminate the need to interpolate in the tables for some cases, we also include recommendations for k/k_∞ or k/k_o values at 0.1, 1.0 and 10 atmospheres for N_2 or Ar and the reactant itself (model for strong collider) in the higher temperature region.

Finally, for each reaction we give the references used in the evaluation, the evaluator and the date. Hopefully, all the literature on this reaction previous to this date has been accessed. The author will be grateful to readers who will bring to his attention publications that have been inadvertently omitted.

1.5. Guide to Thermodynamic and Transport Tables

This section contains thermodynamic and transport properties of methanol and the hydroxymethyl radical. For the thermodynamic properties, the temperature range covered is from 300–1500 K. The properties tabulated include heat capacity, entropy, enthalpy of formation and Gibbs free energy of formation. In addition, we give a polynomial fit of the logarithm of the equilibrium constant of formation. The sources for this data can be found in a footnote. The transport properties are of use for evaluation of fall-off behavior. We therefore include the collision cross-section and the Lennard-Jones well depth.

1.6. Acknowledgments

This work was supported by the Department of Energy, Division of Basic Energy Sciences and the Office of Standard Reference Data, National Bureau of Standards. We are grateful to Dr. John T. Herron, Dr. R. J. Cvetanovic and Ms. Rhoda Levin for their careful reading of the manuscript. We are indebted to Ms. Rhoda Levin and Mrs. Geraldine Zumwalt for their attention to many of the details of editing, keyboarding and the preparation of the manuscript.

1.7. References to the Introduction

[1] W. Tsang and R. F. Hampson, J. Phys. Chem. Ref. Data **15**, 1087 (1986).
[2] See references in Data Tables.
[3] C. K. Westbrook and F. L. Dryer, "A Comprehensive Mechanism for Methanol Oxidation," Combust. Sci. Tech. **20**, 125 (1979).
[4] H. S. Johnston, *Gas Phase Reaction Rate Theory* (Ronald Press, New York, 1966).
[5] P. J. Robinson and K. A. Holbrook, *Unimolecular Reactions* (Wiley–Interscience, New York, 1972).
[6] J. Troe, "Theory of Unimolecular Reactions at Low Pressure: I: Solutions of the Master Equations, II: Strong Collision Rate Constant Applications," J. Chem. Phys. **66**, 4725, 4758 (1977).
[7] R. C. Reid, J. M. Prausnitz, and T. K. Sherwood, *The Properties of Gases and Liquids*, 3rd ed. (McGraw–Hill, New York, 1977).

2. Index of Reactions and Summary of Recommended Rate Expressions

No.	Reaction	Rate Constant k/cm^3 $molecule^{-1}s^{-1}$	Uncertainty factor	Page
38,1	$CH_3OH \rightarrow CH_3 + OH$	$k_\infty=1.9\times10^{16}\exp(-46192/T)s^{-1}$ $k/k_\infty=0.312-6.20\times10^{-4}T-2.56\times10^{-7}T^2$ (1 atm, N_2, >900K)	2	478
38,3	$CH_3OH + O_2 \rightarrow CH_2OH + HO_2$	$3.4\times10^{-11}\exp(-22600/T)$	10	481
38,4	$CH_3OH + H \rightarrow CH_2OH + H_2$ (a) $\rightarrow CH_3O + H_2$ (b)	$k_{a+b}=3.52\times10^{-17}T^{2.1}\exp(-2450/T)$	1.5 to 600K, 3 at 2000K	481
		$k_a/k_b=4$	3	
38,5	$CH_3OH + O \rightarrow CH_2OH + OH$ (a) $\rightarrow CH_3O + OH$ (b)	$k_{a+b}=6.44\times10^{-19}T^{2.5}\exp(-1550/T)$ $k_a>k_b$	1.3 to 750K, 2 at 1100K	483
38,6	$CH_3OH + OH \rightarrow CH_2OH + H_2O$ (a)	$k_{a+b}=1.1\times10^{-19}T^{2.5}\exp(483/T)$	1.1 at 300K, 3 at 2000K	485
	$\rightarrow CH_3O + H_2O$ (b)	$k_a/k_b=3.7\exp(-1020/T)$	1.6 to 500K	
38,7	$CH_3OH + HO_2 \rightarrow CH_2OH + H_2O_2$	$1.6\times10^{-13}\exp(-6330/T)$	10	487
38,15	$CH_3OH + HCO \rightarrow CH_2OH + H_2CO$	$1.6\times10^{-20}T^{2.9}\exp(-6596/T)$	10	487
38,16	$CH_3OH + CH_3 \rightarrow CH_2OH + CH_4$ (a) $\rightarrow CH_3O + CH_4$ (b)	$k_a=5.3\times10^{-23}T^{3.2}\exp(-3609/T)$ $k_b=2.4\times10^{-23}T^{3.1}\exp(-3490/T)$	1.4 to 600K, 3 at 2000K	488
38,17	$CH_3OH + C_2H_5 \rightarrow CH_2OH + C_2H_6$ (a) $\rightarrow CH_3O + C_2H_6$ (b)	$k_a=5.3\times10^{-23}T^{3.2}\exp(-4610/T)$ $k_b=2.4\times10^{-23}T^{3.1}\exp(-4500/T)$	3 3	489
38,19	$CH_3OH + C_2H_3 \rightarrow CH_2OH + C_2H_4$ (a) $\rightarrow CH_3O + C_2H_4$ (b)	$k_a=5.3\times10^{-23}T^{3.2}\exp(-3609/T)$ $k_b=2.4\times10^{-23}T^{3.1}\exp(-3490/T)$	10 10	489
38,21	$CH_3OH + C_2H \rightarrow CH_2OH + C_2H_2$ (a) $\rightarrow CH_3O + C_2H_2$ (b)	$k_a=1\times10^{-11}$ $k_b=2\times10^{-12}$	5 5	490
38,22	$CH_3OH + CH_3CO \rightarrow CH_2OH + CH_3CHO$	$8.06\times10^{-21}T^3\exp(-6210/T)$	3	490
38,23	$CH_3OH + CH_3OO \rightarrow CH_2OH + CH_3OOH$	$3\times10^{-13}\exp(-6900/T)$	1.3 at 600K, increasing to 2 at 1000K	491
38.24	$CH_3OH + CH_3O \rightarrow CH_2OH + CH_3OH$	$5\times10^{-13}\exp(-2050/T)$	10	491
38,25	$CH_3OH + {}^1CH_2 \rightarrow CH_3 + CH_2OH$	2.5×10^{-12}	3	492

2. **Index of Reactions and Summary of Recommended Rate Expressions** -- Continued

No.	Reaction	Rate Constant $k/cm^3\ molecule^{-1}s^{-1}$	Uncertainty factor	Page
38,26	$CH_3OH + {}^3CH_2 \rightarrow CH_2OH + CH_3$ (a)	$k_a=5.3\times10^{-23}T^{3.2}\exp(-3609/T)$	3	493
	$\rightarrow CH_3O + CH_3$ (b)	$k_b=2.4\times10^{-23}T^{3.1}\exp(-3490/T)$	3	
39,1	$CH_2OH + M \rightarrow H + HCHO + M$	$k_o=75T^{-2.5}\exp(-17205/T)$	4	494
		$k(N_2,\ >900K)=1.9\times10^{19}T^{-8}\exp(-21645/T)$ (strong collider)	4	
39,2	$CH_2OH + H_2 \rightarrow CH_3OH + H$	$1.12\times10^{-18}T^{2.0}\exp(-6722/T)$	4	495
39,3	$CH_2OH + O_2 \rightarrow HCHO + HO_2$	2.0×10^{-12}	2	495
39,4	$CH_2OH + H \rightarrow HCHO + H_2$ (a)	$k_a=1\times10^{-11}$	2	496
	$\rightarrow CH_3 + OH$ (b)	$k_b=1.6\times10^{-10}$	2	
39,5	$CH_2OH + O \rightarrow HCHO + OH$	7×10^{-11}	2	497
39,6	$CH_2OH + OH \rightarrow HCHO + H_2O$	4×10^{-11}	2	497
39,7	$CH_2OH + HO_2 \rightarrow HCHO + H_2O_2$	2×10^{-11}	2	498
39,8	$CH_2OH + H_2O_2 \rightarrow CH_3OH + HO_2$	$5\times10^{-15}\exp(-1300/T)$	10	498
39,10	$CH_2OH + CH_4 \rightarrow CH_3OH + CH_3$	$3.6\times10^{-23}T^{3.1}\exp(-8166/T)$	3	498
39,11	$CH_2OH + C_2H_6 \rightarrow CH_3OH + C_2H_5$	$3.3\times10^{-22}T^{3}\exp(-7033/T)$	5	499
39,12	$CH_2OH + HCHO \rightarrow CH_3OH + HCO$	$9.1\times10^{-21}T^{2.8}\exp(-2950/T)$	3	499
39,15	$CH_2OH + HCO \rightarrow CH_3OH + CO$ (a)	$k_a=2\times10^{-10}$	3	500
	$\rightarrow 2HCHO$ (b)	$k_b=3\times10^{-10}$	3	
39,16	$CH_2OH + CH_3 \rightarrow CH_3CH_2OH$ (a)	$k_{a\infty}=2\times10^{-11}$ $\log(k_a/k_{a\infty})=0.202+1.755\times10^{-4}T-5.61\times10^{-7}T^2$ (1 atm N_2, >900K)	2	500
	$\rightarrow CH_4 + HCHO$ (b)	$k_b=4\times10^{-12}$	5	
39,17	$CH_2OH + C_2H_5 \rightarrow n\text{-}C_3H_7OH$ (a)	$k_a=2\times10^{-11}$	2	502
	$\rightarrow C_2H_6 + HCHO$ (b)	$k_b=4\times10^{-12}$	5	
	$\rightarrow C_2H_4 + CH_3OH$ (c)	$k_c=4\times10^{-12}$	5	
39,18	$CH_2OH + C_2H_4 \rightarrow (CH_2)_3OH$ (a)	$k_a=8\times10^{-14}\exp(-3500/T)$ (reversed under combustion conditions)		502
	$\rightarrow C_2H_5 + HCHO$ (b)	$k_b=k_a x(\exp(-2000/T)/(1+\exp(-2000/T)))$	5	

2. **Index of Reactions and Summary of Recommended Rate Expressions** -- Continued

No.	Reaction	Rate Constant k/cm^3 molecule$^{-1}s^{-1}$	Uncertainty factor	Page
39,19	$CH_2OH + C_2H_3 \rightarrow C_2H_4 + HCHO$ (a)	$k_a=5x10^{-11}$	2.5	503
	$\rightarrow C_3H_5 + OH$ (b)	$k_b=2x10^{-11}$	2	
39,20	$CH_2OH + C_2H_2 \rightarrow C_3H_4OH$	$1.2x10^{-12}exp(-4531/T)$	3	503
39,21	$CH_2OH + C_2H \rightarrow C_2H_2 + HCHO$ (a)	$k_a=6x10^{-11}$	5	504
	$\rightarrow C_3H_3 + OH$ (b)	$k_b=2x10^{-11}$	3	
39,22	$CH_2OH + CH_3CO \rightarrow CH_3COCH_2OH$	$2x10^{-11}$	2	504
39,23	$CH_2OH + CH_3OO \rightarrow CH_3O + OH + HCHO$	$2x10^{-11}$	3	504
39,24	$CH_2OH + CH_3O \rightarrow CH_3OH + HCHO$	$4x10^{-11}$	2	505
39,25	$CH_2OH + {}^1CH_2 \rightarrow CH_3CHO + H$	$3x10^{-11}$	2	505
39,26	$CH_2OH + {}^3CH_2 \rightarrow C_2H_4 + OH$ (a)	$k_a=4x10^{-11}$	3	505
	$\rightarrow CH_3 + HCHO$ (b)	$k_b=2x10^{-12}$	3	
39,38	$CH_2OH + CH_3OH \rightarrow CH_3OH + CH_3O$	$1.3x10^{-14}exp(-6070/T)$	10	506
39,39	$CH_2OH + CH_2OH \rightarrow HOCH_2CH_2OH$ (a)	$k_a=1.6x10^{-11}$	2	506
	$\rightarrow CH_3OH + HCHO$ (b)	$k_b=8x10^{-12}$	2	

3. Chemical Kinetic Data Tables

38,1 $CH_3OH \rightarrow CH_3 + OH$

Reference	Conditions		Reaction rate constant,	Uncertainty
	Temp./K	[M]/molecule cm^{-3}	$k/cm^3molecule^{-1}s^{-1}$	factor
log K_p = 8.04602 - 20660.1/T + 67609.5/T^2				
Cribb, et al. (1984)	1800-2660	$1-1.3x10^{18}$ Ar and N_2. (Shock tube, laser schlieren and mass spec.)	$k=8.5x10^{18}T^{-7.08}exp(-45317/T)$	2
Spindler, Wagner (1982)	1600-2100	$8.0-200.0x10^{17}$ Ar. (Shock tube, CH_3, OH detection)	$k\infty \simeq 9.4x10^{15}exp(-45250/T)s^{-1}$ $k_o(Ar) = 3.3x10^{-7}exp(-34420/T)$	
Tsuboi, et al. (1981)	1500-1900	$6.0x10^{18}$ Ar.	$6.0x10^{12}exp(-37310/T)s^{-1}$	3
		$3.0x10^{19}$ Ar.	$3.6x10^{13}exp(-37788/T)s^{-1}$	3
		$6.0x10^{19}$ Ar. 0.01 - 1% CH_3OH. (Shock tube, UV absorption and IR emission)	$8.7x10^{13}exp(-38270/T)s^{-1}$	
Westbrook, Dryer (1979)	1000-2200	$3.7x10^{18}$ N_2 (Modeling flow reactor, and shock tube results)	$5.0x10^{-6}exp(-40280/T)$	
Bowman (1975)	1500-2200	$6.0-17.0x10^{18}$ Ar, 0.75 to 4% CH_3OH. (Shock tube, optical detection of OH, O, H_2O)	$6.7x10^{-9}exp(-34200/T)$	3
Recommended value			$k\infty=1.9x10^{16}exp(-46192/T)s^{-1}$	2
Recommended value	>900	1 atm, N_2	$\log k/k\infty=0.312-6.20x10^{-4}T-2.56x10^{-7}T^2$	

Comments and Recommendations

The experimental results under almost identical experimental conditions vary by a factor of 30. The results of Westbrook and Dryer and of Spindler and Wagner are in agreement suggesting that the collision efficiencies for N_2 and Argon are similar. The rate constants of Bowman are a factor of 10 lower than those of Spindler and Wagner, while those of Tsuboi are a factor of 3 higher. The results of Cribb et al. occupy an intermediate position between the latter two results. We have fitted the data on the basis of the work of Spindler and Wagner, Cribb et al., Tsuboi, and Westbrook and Dryer, and the measured rate for the reverse process at room temperature (See Rn. 16,6 in Part 1). This leads to a step size down for argon of 500 cm^{-1} and a high pressure rate expression of

$$k(CH_3OH \rightarrow CH_3 + OH) = 1.9x10^{16}exp(-46192/T)s^{-1}$$

The results of Bowman lead to a step size down of 160 cm^{-1} and is incompatible with the other measurements. Fall-off behavior on a strong collision basis can be found in Table A. Collision efficiencies as a function of temperature and step size down can be found in Table B. Fall-off behavior at 0.1, 1.0 and 10 atm in argon and CH_3OH over the range of 900-2500 K is as follows:

$$\log(k(A,\ 0.1)/k\infty) = 0.574 - 1.64\text{x}10^{-3}T - 3.54\text{x}10^{-8}T^2$$

$$\log(k(A,\ 1.0)/k\infty) = 0.312 - 6.20\text{x}10^{-4}T - 2.56\text{x}10^{-7}T^2$$

$$\log(k(A,\ 10)/k\infty) = 4.39\text{x}10^{-2} + 1.13\text{x}10^{-4}T - 3.66\text{x}10^{-7}T^2$$

$$\log(k(CH_3OH,\ 0.1)/k\infty) = 0.452 - 1.20\text{x}10^{-3}T - 1.12\text{x}10^{-7}T^2$$

$$\log(k(CH_3OH,\ 1.0)/k\infty) = 0.193 - 3.00\text{x}10^{-4}T - 2.88\text{x}10^{-7}T^2$$

$$\log(k(CH_3OH,\ 10)/k\infty) = -2.40\text{x}10^{-2} + 2.39\text{x}10^{-4}T - 3.35\text{x}10^{-7}T^2$$

where we have assumed a step size down of 500 cm^{-1} and 1000 cm^{-1} respectively. The uncertainty in the rate constant is a factor of 2.

Table A. log(k/k∞) as a function of concentration and temperature for CH_3OH decomposition assuming strong collisions

log[M]	T/K											
	300	500	700	900	1100	1300	1500	1700	1900	2100	2300	2500
16.0	-0.54	-0.94	-1.3	-1.62	-1.90	-2.12	-2.37	-2.6	-2.81	-3.02	-3.21	-3.39
16.5	-0.32	-0.64	-0.95	-1.24	-1.50	-1.70	-1.94	-2.16	-2.36	-2.56	-2.75	-2.92
17.0	-0.17	-0.40	-0.66	-0.9	-1.13	-1.22	-1.54	-1.75	-1.94	-2.12	-2.31	-2.47
17.5	-0.08	-0.23	-0.42	-0.62	-0.82	-0.98	-1.18	-1.36	-1.54	-1.72	-1.80	-2.04
18.0	-0.03	-0.12	-0.25	-0.39	-0.55	-0.69	-0.86	-1.02	-1.18	-1.34	-1.50	-1.64
18.5	-0.01	-0.05	-0.13	-0.22	-0.33	-0.45	-0.59	-0.72	-0.87	-1.01	-1.14	-1.27
19.0		-0.02	-0.06	-0.11	-0.18	-0.27	-0.37	-0.48	-0.60	-0.72	-0.83	-0.94
19.5		-0.01	-0.02	-0.05	-0.09	-0.15	-0.22	-0.30	-0.38	-0.47	-0.57	-0.66
20.0			-0.01	-0.02	-0.04	-0.07	-0.11	-0.16	-0.22	-0.28	-0.35	-0.42
20.5				-0.01	-0.01	-0.03	-0.05	-0.08	-0.11	-0.15	-0.20	-0.24
21.0						-0.01	-0.02	-0.03	-0.05	-0.07	-0.10	-0.12

Table B. Collision efficiency, β_c, as a function of temperature and step size down for CH_3OH decomposition

T/K	Step-size (cm^{-1})				
	150	300	600	1200	2400
300	0.15	0.32	0.52	0.70	0.83
500	0.08	0.17	0.36	0.57	0.74
700	0.043	0.12	0.26	0.46	0.65
900	0.027	0.079	0.19	0.37	0.58
1100	0.018	0.055	0.15	0.30	0.51
1300	0.012	0.038	0.11	0.24	0.43
1500	0.008	0.028	0.082	0.20	0.38
1700	0.006	0.021	0.064	0.16	0.33
1900	0.0045	0.016	0.050	0.13	0.27
2100	0.0034	0.012	0.039	0.11	0.25
2300	0.0026	0.009	0.031	0.09	0.21
2500	0.002	0.007	0.025	0.074	0.18

Arrhenius plots of the rate constants k_r for $OH + CH_3$ combination (in Argon), the reverse of Rn. 38,1, are given in Fig. 2. The values of k_r were obtained from $k_{38,1}$ and the equilibrium constants of Rn. 38,1. The numbers on the curves are the logarithms of the gas concentration in molec/cm^3.

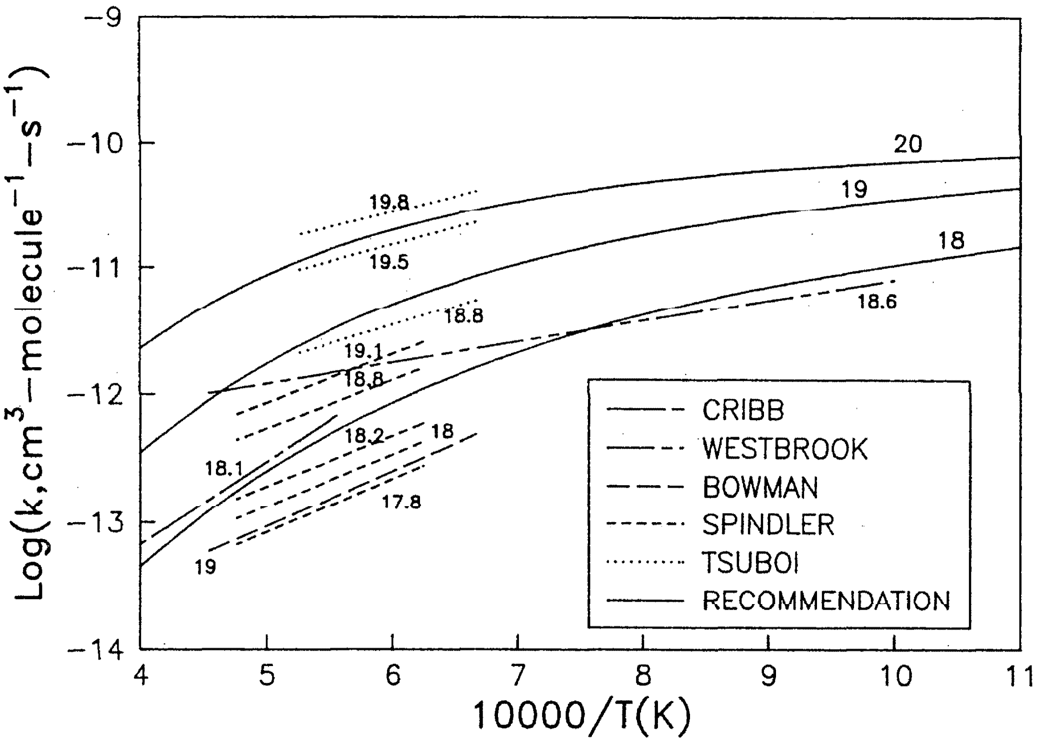

Fig. 2. Arrhenius plots of the rate constants k_r for $OH + CH_3$ combination, the reverse of Rn. 38,1.

(W. Tsang, April 1985)

References

Bowman, C. T., "A Shock-Tube Investigation of the High Temperature Oxidation of Methanol," Combust. Flame 25, 343 (1975)

Cribb, P. H., Dove, J. E., and Yamazaki, S., "A Shock Tube Study of Methanol Pyrolysis," Symp. Combust. 20 (Combustion Institute, Pittsburgh, 1985) p. 779

Spindler, K., and Wagner, H. Gg., "Zum Thermischen Unimolekularen Zerfall von Methanol," Ber. Bunsenges. Phys. Chem. 86, 2 (1982)

Tsuboi, T., Katoh, M., Kikuchi, S., and Hashimoto, K., "Thermal Decomposition of Methanol Behind Shock Waves," Jpn. J. Appl. Phys. 20, 983 (1981)

Westbrook, C. K., and Dryer, F. L., "A Comprehensive Mechanism for Methanol Oxidation," Combust. Sci. Technol. 20, 125 (1979)

38,3 $CH_3OH + O_2 \rightarrow CH_2OH + HO_2$

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, $k/cm^3 molecule^{-1} s^{-1}$	Uncertainty factor
Recommended value			$3.4\times10^{-11}\exp(-22600/T)$	10

Comments and Recommendations

There are no data. We recommend the rate expression $3.4\times10^{-11}\exp(-22600/T)$, with an uncertainty of a factor of 10, based on Walker's estimates for the rate of O_2 attack on hydrocarbons [R.W. Walker, "A Critical Survey of Rate Constants for Reactions in Gas-phase Hydrocarbon Oxidation", in 'Reaction Kinetics', ed. P.G. Ashmore (Specialist Periodical Report), The Chemical Society, London, 1975, Vol. 1, p. 161]
(W. Tsang, April 1985)

38,4 $CH_3OH + H \rightarrow H_2 + CH_2OH$ (a)
$\rightarrow H_2 + CH_3O$ (b)

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, $k/cm^3 molecule^{-1} s^{-1}$	Uncertainty factor
Hoyerman, et al. (1981)	500-680	$0.25-1.0\times10^{17}$ He (Discharge flow - MS)	$k_{a+b} = 2.2\times10^{-11}\exp(-2650/T)$	1.6
Vandooren, Van Tiggelen (1981)	1000-2000	$2-4\times10^{17}$ (Methanol flame, MS-detection)	$k_{a+b} = 5.6\times10^{-11}\exp(-1309/T)$	3
Aders (1973)	298-650	$\sim 2.0\times10^{17}$ (Discharge flow, ESR, MS)	$k_{a+b} = 2.2\times10^{-11}\exp(-2669/T)$	2
Meagher, et al. (1974)	300-404	1.5×10^{16} (Discharge flow, ESR, MS)	$k_{a+b} = 1.1\times10^{-11}\exp(-2739/T)$	3
Recommended value	500-2000		$k_{a+b}=3.52\times10^{-17}T^{2.11}\times \exp(-2450/T)$	1.5 to 600K, 3 at 2000K.
Recommended value			$k_a/k_b=4$	3

Comments and Recommendations

Under most combustion conditions it is immaterial whether the reaction goes by path (a) or (b) since the newly formed radicals should decompose to HCHO and H quite rapidly. Reaction (a) is the most exothermic channel. We have fitted all the results on the basis of BEBO transition state calculations, leading to the recommended rate expression listed above. Uncertainty factor in k_{a+b} is 1.5 up to 600 K and 3 at 2000 K. Arrhenius plots of k_{a+b} are given in Fig. 3. From the data on methyl attack on methanol we estimate k_a/k_b ~ 4 with an uncertainty factor of 3.

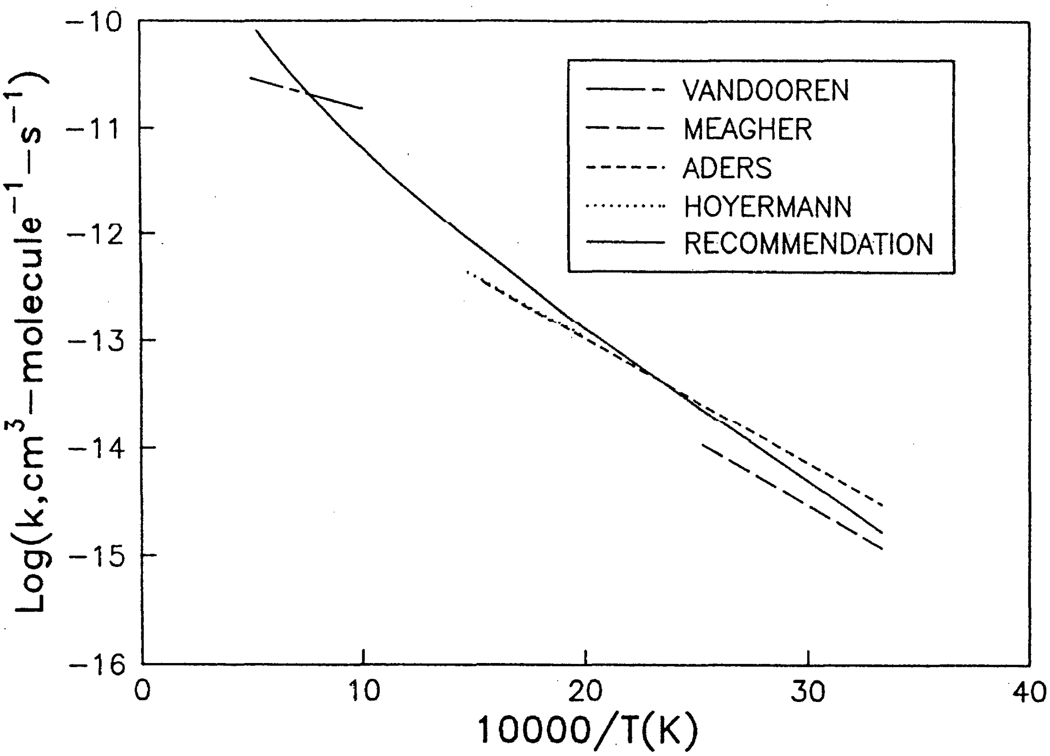

Fig. 3. Arrhenius plots of the rate constants k_{a+b}.

(W. Tsang, April 1985)

References

Aders, W. K., "Reactions of H-Atoms with Alcohols," Combust. Inst., European Symp. (F. Weinberg, ed) Academic Press, London 1, 19 (1973)

Hoyermann, K., Sievert, R., and Wagner, H. Gg., "Mechanism of the Reaction of H Atoms with Methanol," Ber. Bunsenges. Phys. Chem. 85, 149 (1981)

Meagher, J. F., Kim, P., Lee, J. H., and Timmons, R. B., "Kinetic Isotope Effects in the Reactions of Hydrogen and Deuterium Atoms with Dimethyl Ether and Methanol," J. Phys. Chem. 78, 2650 (1974)

Vandooren, J., and Van Tiggelen, P. J., "Experimental Investigation of Methanol Oxidation in Flames: Mechanisms and Rate Constants of Elementary Steps," Symp. Combust 18 (Combustion Institute, Pittsburgh, 1981) p. 473

38,5 $CH_3OH + O \rightarrow OH + CH_2OH$ (a)
$\rightarrow OH + CH_3O$ (b)

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, $k/cm^3molecule^{-1}s^{-1}$	Uncertainty factor
Failes, et al. (1982)	297-544	10^{18} N_2O, CH_3OH, NO, (Hg-photosensitized decomp. of N_2O)	$k_{a+b}=1.63x10^{-11}exp(-2267/T)$	1.2
Keil, et al. (1981)	298-998	$3.0-10.0x10^{16}$ O_2, CH_3OH (Discharge flow) $1.0-3.0x10^{18}$ Ar, O_2, CH_3OH (Flash photolysis)	$k_{a+b}=2.7x10^{-11}exp(-2532/T)$	1.1
Grotheer, Just (1981)	300-1006	$3x10^{16}$ CH_3OH, O_2 (Flow reactor, MS-detection of O atoms)	$k_{a+b}=5.7x10^{-11}exp(-2750/T)$	1.3
Lalo, Vermeil (1981)	298	$3.0x10^{17}$ Ar (Flow reactor, Resonance fluorescence detection of O)	$k_{a+b}=6.0x10^{-17}$	1.2
Owens, Roscoe (1975)	301-451	$3.0x10^{16}$ CH_3OH, O_2 (Flow reactor, O-atoms from O+NO emission)	$k_{a+b}=2.4x10^{-12}exp(-1540/T)$	1.3
LeFevre, et al. (1972)	273-438	$5.0x10^{16}$ Ar (Discharge flow, ESR, MS)	$k_{a+b}=2.8x10^{-12}exp(-1140/T)$	2
Recommended value			$k_{a+b}=6.44x10^{-19}T^{2.5}x$ exp(-1550/T)	1.3 to 750K, 2 at 1100K

Comments and Recommendations

Three of the most recent measurements on the rate of this reaction are in excellent agreement. We have carried out BEBO calculations and adjusted the activation energy to fit the experimental data in the 300-750 K range. The resulting expression is $k_{a+b} = 6.44x10^{-19}T^{2.5}exp(-1550/T)cm^3molecule^{-1}s^{-1}$ with an uncertainty factor of 1.3 in the 300-750 K range and increasing to a factor of 2 at 1100 K. Reaction (a) is the exothermic channel and there are three available hydrogens. It is probably the preferred route under most conditions. Arrhenius plots of k_{a+b} are given in Fig.4.

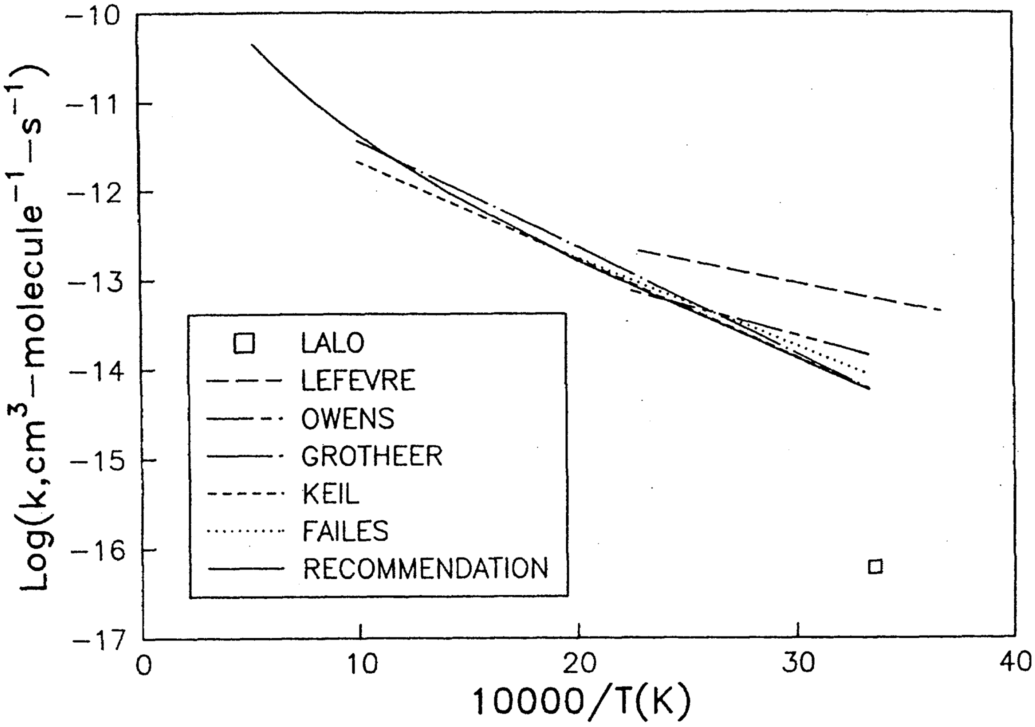

Fig. 4. Arrhenius plots of the rate constants k_{a+b}.
(W. Tsang, April 1985)

References

Failes, R. L., Singelton, D. L., Paraskevopoulos, G., and Irwin, R. S., "Rate Constants for the Reaction of Ground-State Oxygen Atoms with Methanol from 297 to 544 K," Int. J. Chem. Kinet. 14, 371 (1982)

Grotheer, H. H., and Just, Th., "Kinetics of the Oxidation of Methanol by Ground-State Atomic Oxygen," Chem. Phys. Lett. 78, 71 (1981)

Keil, D. G., Tanzawa, T., Skolnik, E. G., Klemm, R. B., and Michael, J. V., "Rate Constants for the Reaction of Ground State Atomic Oxygen with Methanol," J. Chem. Phys. 75, 2693 (1981)

Lalo, C., and Vermeil, C., "Constante de Vitesse A 298 K de la Reaction d'Oxydation du Methanol par l'Oxygene Atomique," J. Chim. Phys. 77, 131 (1980)

LeFevre, H. F., Meagher, J. F., and Timmons, R. B., "The Kinetics of the Reactions of O(^{3}P) Atoms with Dimethyl Ether and Methanol" Int. J. Chem. Kinet. 4, 103 (1972)

Owens, C. M., and Roscoe, J. M., "The Reactions of Atomic Oxygen with Methanol and Ethanol," Can. J. Chem. 54, 984 (1976)

38,6 $CH_3OH + OH \rightarrow CH_2OH + H_2O$ (a)
$\rightarrow CH_3O + H_2O$ (b)

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, $k/cm^3molecule^{-1}s^{-1}$	Uncertainty factor
Meier, et al. (1984,1985)	300-1000	$0.5\text{-}5x10^{18}$ He, trace methanol. (Laser induced fluorescence, mass. spec.)	$k_{a+b}=1.1x10^{-11}exp(-718/T)$ $k_a/k_{a+b}=0.21\pm0.1$	1.1
Hagele, et al. (1983)	295-420	$3.0x10^{17}$ He, trace of CH_3OH, HNO_3. (OH from HNO_3, LPRF)	$k_{a+b} = 1.2x10^{-11}exp(-810/T)$ $k_b/k_{a+b} = 0.11\pm0.03$ (298K) $k_b/k_{a+b} = 0.22\pm0.07$ (393K)	1.1
Vandooren, Van Tiggelen (1981)	1100-2000	$2.5x10^{17}$ (methanol flame)	$k_{a+b} = 8.0x10^{-11}exp(-2266/T)$	3
Ravishankara, Davis (1978)	298	$1.2x10^{18}$ He (Flash photolysis, resonance fluorescence)	$k_{a+b} = 1.0x10^{-12}$	1.1
Overend, Paraskevopoulos (1978)	296	$1.6x10^{18}$, H_2, 10% N_2O; also OH from H_2O in He (Flash photolysis, Resonance absorption)	$k_{a+b} = 1.06x10^{-12}$	1.1
Campbell, et al. (1976)	292	$3.0x10^{18}$, ~ 1% NO_2, 0.1% H_2O_2 in CO (Static)	$k_{a+b} = 0.95x10^{-12}$	1.1
Osif, et al. (1975)	298	$(8.0\text{-}60.0)x10^{17}$, CH_3OH, N_2O, CO	$k_{a+b} = 9.6x10^{-14}$	1.2
	345		$k_{a+b} = 1.6x10^{-13}$	
Recommended value			$k_{a+b}=1.1x10^{-19}T^{2.53}x$ exp(483/T)	1.1 at 300K, 3 at 2000K.
Recommended value			$k_a/k_b=3.7exp(-1020/T)$	1.6 to 500K

Comments and Recommendations

The room temperature values for this reaction are very well established from direct determinations. Using BEBO calculations, we recommend the rate expression:

$$k_{a+b} = 1.1x10^{-19}T^{2.53}exp(-483/T)cm^3molecule^{-1}s^{-1}$$

with an uncertainty factor of 1.1 at room temperature and of 2 at 2000 K. Note that this expression goes smoothly through the high temperature results. The Arrhenius plots of k_{a+b} are given in Fig. 5. The work of Hagele et al. leads to $k_b/k_a = 3.7exp(-1020/T)$. The results of Meier et al. suggest that the branching ratio is subject to considerable uncertainty.

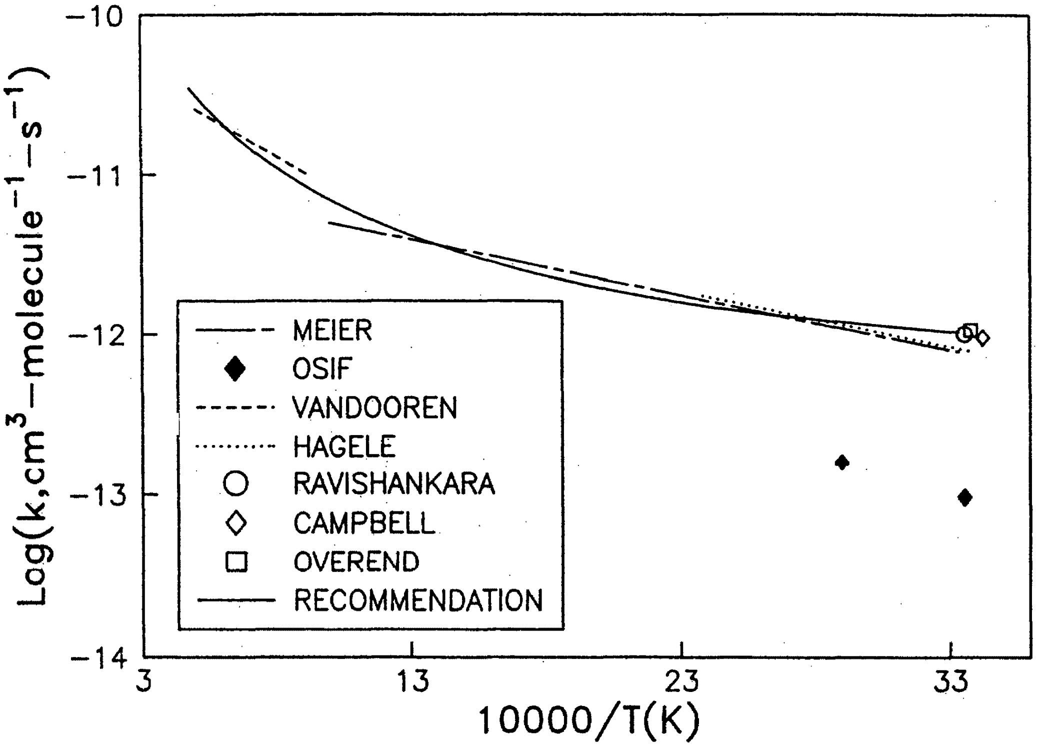

Fig. 5. Arrhenius plots of the rate constants k_{a+b}.

(W. Tsang, April 1985)

References

Campbell, I. M., McLaughlin, D. F., and Handy, B. J., "Rate Constants for Reactions of Hydroxyl Radicals with Alcohol Vapors at 292 K," Chem. Phys. Lett. 39, 362 (1976)

Hagele, J., Lorenz, K., Rhasa, D., and Zellner, R., "Rate Constants and CH_3O Product Yield of the Reaction $OH + CH_3OH \rightarrow$ Products," Ber. Bunsenges. Phys. Chem. 87, 1023 (1983)

Meier, V., Grotheer, H. H., and Just., T., "Temperature Dependence and Ratio of the CH_3OH Reaction," Chem. Phys. Lett. 106, 97 (1984)

Meier, V., Grotheer, H. H., Rickert, G., and Just, T., "Study of Hydroxyl Radical Reaction with Methanol and Ethanol by Laser Induced Fluorescence," Ber. Bunsenges. Phys. Chem. 89, 325 (1985)

Osif, T. L., "Reactions of the Singlet D Oxygen Atom and the Hydroxyl Radical with Methanol, Oxidation of the Formyl Radical, and the Photochemical Oxidation of Formaldehyde," Diss. Abstr. Int. B 37, 5659 (1977)

Osif, T. L., Simonaitis, R., and Heicklen, J., "The Reactions of $O(^1D)$ and HO with CH_3OH," J. Photochem. 4, 233 (1975)

Overend, R., and Paraskevopoulos, G., "Rates of OH Radical Reactions. 4. Reactions with Methanol, Ethanol, 1-Propanol, and 2-Propanol at 296 K," J. Phys. Chem. 82, 1329 (1978)

Ravishankara, A. R., and Davis, D. D., "Kinetic Rate Constants for the Reaction of OH with Methanol, Ethanol, and Tetrahydrofuran at 298K," J. Phys. Chem. 82 2852 (1978)

Vandooren, J., and Van Tiggelen, P. J., "Experimental Investigation of Methanol Oxidation in Flames: Mechanisms and Rate Constants of Elementary Steps," Symp. Combust. 18 (Combustion Institute, Pittsburgh, 1981) p. 473

38,7 $CH_3OH + HO_2 \rightarrow H_2O_2 + CH_2OH$ (a)

$\rightarrow H_2O_2 + CH_3O$ (b)

	Conditions		Reaction rate constant,	Uncertainty
Reference	Temp./K	[M]/molecule cm^{-3}	$k/cm^3molecule^{-1}s^{-1}$	factor
Recommended value			k_a=1.6x10^{-13}exp(-6330/T)	10

Comments and Recommendations

There are no data. We suggest the use for k_a of the same rate expression as recommended by Walker [R.W. Walker, "Rate Constants for Reactions in Gas Phase Hydrocarbon Oxidation", in 'Gas Kinetics and Energy Transfer', ed. P.G. Ashmore and R.J. Donovan (Specialist Periodical Reports), The Chemical Society, London, 1977, Vol. 2, p. 296] for $HO_2 + C_3H_8 \rightarrow i\text{-}C_3H_7 + H_2O_2$, i.e.

$$k_a = 1.6x10^{-13}exp(-6330/T)cm^3molecule^{-1}s^{-1}$$

The uncertainty is a factor of 10. The exothermicity of the abstraction process will make (a) the favored channel. Reaction (b) is endothermic.

(W. Tsang, April 1985)

38,15 $CH_3OH + HCO \rightarrow CH_2OH + H_2CO$ (a)

$\rightarrow CH_3O + H_2CO$ (b)

	Conditions		Reaction rate constant,	Uncertainty
Reference	Temp./K	[M]/molecule cm^{-3}	$k/cm^3molecule^{-1}s^{-1}$	factor
log K_p(a) = 0.56121 - 1639.5/T + 9487/T^2 - 364000/T^3				
log K_p(b) = -1.0002 - 3456.7/T + 58603/T^2 - 1.08x10^7/T^3				
Recommended value			k_a=1.6x$10^{-20}$$T^{2.90}$exp(-6596/T)	10

Comments and Recommendations

There are no data. We have used the equilibrium constant and the estimated rate expression for the reverse reaction (39,12) to obtain the following value for k_a

$$k_a=1.6x10^{-20}T^{2.90}exp(-6596/T)cm^3molecule^{-1}s^{-1}$$

with an uncertainty of a factor of 10. The rate constant of the second channel is estimated to be a factor of 100 or more slower on the basis of the reverse process, CH_3O + HCHO (24,12), and the equilibrium constant.

(W. Tsang, May 1985)

38,16 $CH_3OH + CH_3 \rightarrow CH_4 + CH_2OH$ (a)
$\rightarrow CH_4 + CH_3O$ (b)

	Conditions		Reaction rate constant,	Uncertainty
Reference	Temp./K	[M]/molecule cm^{-3}	$k/cm^3molecule^{-1}s^{-1}$	factor
Spindler, Wagner (1982)	1600-2100	$0.6\text{-}33.0x10^{18}$ Ar (Shock tube, CH_3 absorption in CH_3OH decomp.)	$k_{a+b} = 1.5x10^{-11}exp(-4940/T)$	2
Kerr, Parsonage (1976) (review)	350-550		$k_a = 3.24x10^{-13}exp(-5035/T)$ $k_b = 1.0x10^{-13}exp(-4884/T)$	1.4
Recommended value			$k_a=5.3x10^{-23}T^{3.17}x$ $exp(-3609/T)$	1.4 to 600K,
Recommended value			$k_b=2.4x10^{-23}T^{3.1}exp(-3490/T)$	3 at 2000K

Comments and Recommendations

Using the results of Kerr and Parsonage and of a BEBO calculation, we suggest:

$k_b = 2.4x10^{-23}T^{3.1}exp(-3490/T)cm^3molecule^{-1}s^{-1}$, and

$k_a = 5.3x10^{-23}T^{3.17}exp(-3609/T)cm^3molecule^{-1}s^{-1}$

with an uncertainty factor of 1.4 up to 600 K and increasing to 3 at 2000 K. Arrhenius plots of k_a and k_b are given in Fig. 6.

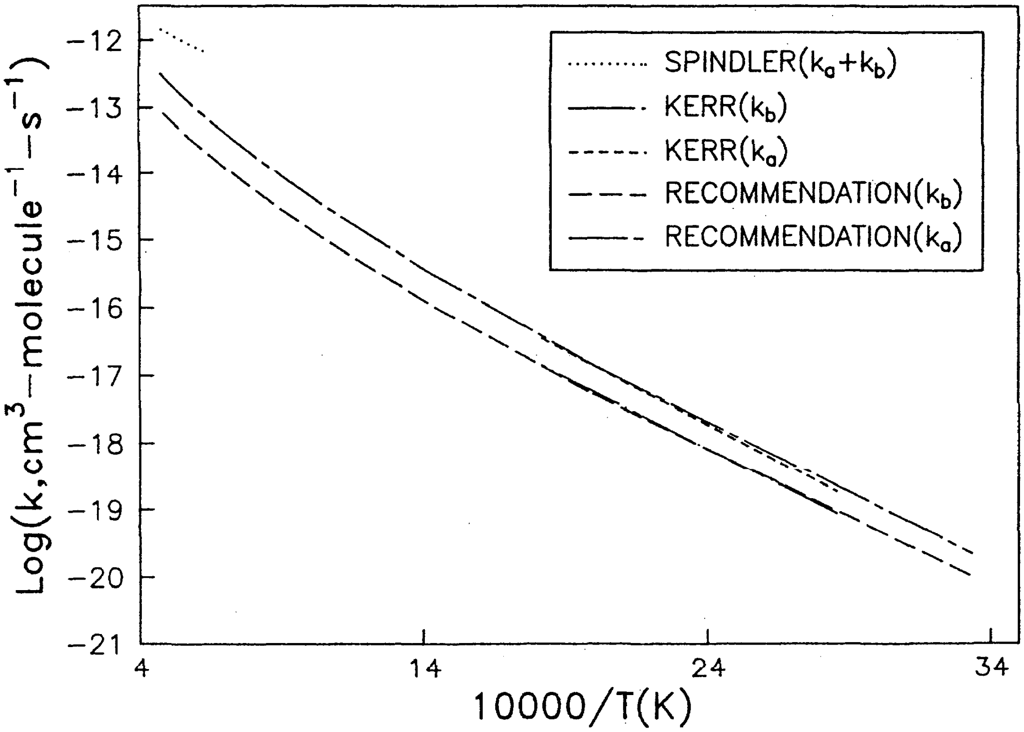

Fig. 6. Arrhenius plots of the rate constants k_a and k_b.

(W. Tsang, April 1985)

References

Spindler, K., and Wagner, H. Gg., "Zum Thermischen Unimolekularen Zerfall von Methanol," Ber. Bunsenges. Phys. Chem. 86, 2 (1982)

Kerr, J. A., and Parsonage, M. J., "Evaluated Kinetic Data on Gas Phase Hydrogen Transfer Reactions of Methyl Radicals," (Butterworths, London, 1976) p. 95

38,17 $CH_3OH + C_2H_5 \rightarrow C_2H_6 + CH_2OH$ (a)
$\rightarrow C_2H_6 + CH_3O$ (b)

Reference	Conditions Temp./K	 $[M]$/molecule cm^{-3}	Reaction rate constant, $k/cm^3molecule^{-1}s^{-1}$	Uncertainty factor
Recommended value			$k_a=5.3x10^{-23}T^{3.17}exp(-4610/T)$	3
Recommended value			$k_b=2.4x10^{-23}T^{3.1}exp(-4500/T)$	3

Comments and Recommendations

There are no data. However, ethyl radicals are known to be considerably less reactive than methyl. We suggest the use of the rate expressions:

$k_a = 5.3x10^{-23}T^{3.17}exp(-4610/T)cm^3molecule^{-1}s^{-1}$ and

$k_b = 2.4x10^{-23}T^{3.1}exp(-4500/T)cm^3molecule^{-1}s^{-1}$.

This is based on the reaction of CH_3 with CH_3OH (38,16) and the observed trends in reactivity of methyl and ethyl radicals with hydrocarbons. The uncertainties are a factor of 3.

(W. Tsang, April 1985)

38,19 $CH_3OH + C_2H_3 \rightarrow C_2H_4 + CH_3O$ (a)
$\rightarrow C_2H_4 + CH_3O$ (b)

Reference	Conditions Temp./K	 $[M]$/molecule cm^{-3}	Reaction rate constant, $k/cm^3molecule^{-1}s^{-1}$	Uncertainty factor
Recommended value			$k_a=5.3x10^{-23}T^{3.17}exp(-3609/T)$	10
Recommended value			$k_b=2.4x10^{-23}T^{3.1}exp(-3490/T)$	10

Comments and Recommendations

There are no data. As a very rough estimate we suggest for reaction (a) the use of our estimated rate expressions for methyl attack on methanol (38,16), i.e. $k_a=5.3x10^{-23}T^{3.17}exp(-3609/T)cm^3molecule^{-1}s^{-1}$, and $k_b=2.4x10^{-23}T^{3.1}exp(-3490/T)$ $cm^3molecule^{-1}s^{-1}$. The uncertainties are a factor of 10.

(W. Tsang, May 1985)

38,21 $CH_3OH + C_2H \rightarrow C_2H_2 + CH_2OH$ (a)
$\rightarrow CH_3O + C_2H_2$ (b)

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, $k/cm^3 molecule^{-1} s^{-1}$	Uncertainty factor
Recommended value			$k_a = 1 \times 10^{-11}$	5
Recommended value			$k_b = 2 \times 10^{-12}$	5

Comments and Recommendations

There are no data. We suggest for this reaction the following rate expressions:

$k_a = 1.0 \times 10^{-11} cm^3 molecule^{-1} s^{-1}$ and

$k_b = 2.0 \times 10^{-12} cm^3 molecule^{-1} s^{-1}$

with uncertainties of a factor of 5. Our estimates are based on measurements of C_2H attack on CH_4 (21,10) and C_2H_6 (21,11).

(W. Tsang, May 1985)

38,22 $CH_3OH + CH_3CO \rightarrow CH_3CHO + CH_2OH$

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, $k/cm^3 molecule^{-1} s^{-1}$	Uncertainty factor
$\log K_p = 0.54426 - 1463.33/T - 19906/T^2 + 6.0754 \times 10^6/T^3$				
Recommended value			$8.06 \times 10^{-21} T^{2.99} \exp(-6210/T)$	3

Comments and Recommendations

There are no data. Using our estimate for the reverse rate, which should be typical for the attack of alkyl radicals on an aldehydic hydrogen, and the equilibrium constant we find

$k(CH_3OH + CH_3CO \rightarrow CH_3CHO + CH_2OH) = 8.06 \times 10^{-21} T^{2.99} \exp(-6210/T) cm^3 molecule^{-1} s^{-1}$.

We estimate an uncertainty of a factor of 3. As expected, the rate constants are very similar to those for HCO attack on methanol. Hydroxy hydrogen abstraction should be much slower and will not be important under combustion conditions.

(W. Tsang, May 1985)

38,23 $CH_3OH + CH_3O_2 \rightarrow CH_3OOH + CH_2OH$

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, $k/cm^3molecule^{-1}s^{-1}$	Uncertainty factor
Anastasi, Hancock (1984)	600	$5.0x10^{18}$ N_2, acetone, oxygen, methanol.	$3.2x10^{-18}$	
Recommended value			$3x10^{-13}exp(-6900/T)$	1.3 at 600K, increasing to 2 at 1000K

Comments and Recommendations

Assuming an A-factor of $3.0x10^{-13}cm^3molecule^{-1}s^{-1}$ we obtain the rate expression

$$k(CH_3O_2 + CH_3OH \rightarrow CH_3OOH + CH_2OH) = 3.0x10^{-13}exp(-6900/T)cm^3molecule^{-1}s^{-1}$$

We estimate the uncertainty to be a factor of 1.3 at 600 K, increasing to a factor of 2 at 1000 K.

(W. Tsang, May 1985)

References

Anastasi, C., and Hancock, D. U., "Reaction of Methylperoxy Radicals with Methanol and Formaldehyde at 600K," J. Chem. Soc., Faraday Trans. I 80, 935 (1984)

38,24 $CH_3OH + CH_3O \rightarrow CH_3OH + CH_2OH$

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, $k/cm^3molecule^{-1}s^{-1}$	Uncertainty factor
Recommended value			$5x10^{-13}exp(-2050/T)$	10

Comments and Recommendations

There are no data. We recommend for this reaction the use of the rate expression $5.0x10^{-13}exp(-2050/T)cm^3molecule^{-1}s^{-1}$, which is 3 times (1 tertiary hydrogen vs. 3 in HCH_2OH) attack on isobutane (J.A. Kerr and S.J. Moss, Handbook of Bimolecular and Termolecular Gas Reactions, Vol I, CRC Press, Boca Raton, FL, 1981). The uncertainty is a factor of 10.

(W. Tsang, May 1985)

38,25 $CH_3OH + {}^1CH_2 \rightarrow C_2H_5OH$ (a)
$\rightarrow CH_3 + CH_2OH$ (b)

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, $k/cm^3molecule^{-1}s^{-1}$	Uncertainty factor
Recommended value			$2.5x10^{-12}$	3

Comments and Recommendations

Although there are no data, there is no doubt that insertion (a) is the main reaction. The hot adduct can dissociate or stabilize. On a strong collision basis the fractional decomposition rates are summarized in Table A. Collision efficiencies can be found in Table B. The absolute rate is estimated to be $2.5x10^{-12}$ $cm^3molecule^{-1}s^{-1}$, with an uncertainty factor of 3. This is based on the rate of ${}^1CH_2$ insertion into the secondary CH_2 bonds in C_3H_8. Under combustion conditions at 0.1, 1.0 and 10 atm, the predominant reaction is decomposition. There is, however, also the possibility of a direct elimination to form $C_2H_4 + H_2O$. We are unable to assess the importance of this channel although we suspect that it will not make any larger contribution than a bond dissociation reaction. Note that the abstraction process (b) will yield the same products as decomposition.

Table A. $\log(k_b/k_{a+b})$ as a function of density and temperature for the insertion of ${}^1CH_2$ in methanol assuming strong collisions

log[M]	T/K 300	 500	 700	 900	 1100	 1300	 1500	 1700	 1900	 2100	 2300	 2500
17.0	-0.02	-0.02	-0.01	-0.01								
17.5	-0.06	-0.04	-0.03	-0.02	-0.01	-0.01						
18.0	-0.16	-0.12	-0.08	-0.06	-0.03	-0.02	-0.01	-0.01	-0.01			
18.5	-0.37	-0.30	-0.20	-0.14	-0.09	-0.06	-0.04	-0.03	-0.02	-0.01	-0.01	-0.01
19.0	-0.71	-0.59	-0.43	-0.31	-0.21	-0.14	-0.10	-0.07	-0.05	-0.03	-0.02	-0.02
19.5	-1.15	-0.98	-0.76	-0.57	-0.42	-0.30	-0.21	-0.15	-0.11	-0.08	-0.06	-0.05
20.0	-1.62	-1.44	-1.18	-0.94	-0.72	-0.55	-0.41	-0.31	-0.24	-0.18	-0.14	-0.11
20.5	-2.11	-1.92	-1.65	-1.36	-1.10	-0.89	-0.70	-0.56	-0.44	-0.37	-0.29	-0.23
21.0	-2.61	-2.41	-2.14	-1.84	-1.55	-1.31	-1.08	-0.90	-0.75	-0.62	-0.52	-0.44

Table B. Collision efficiency, βc, for the decomposition of C_2H_5OH as a function of temperature and step size down

T/K	Step-size (cm^{-1})				
	150	300	600	1200	2400
300	0.15	0.31	0.51	0.69	0.83
500	0.07	0.173	0.35	0.55	0.72
700	0.045	0.124	0.27	0.47	0.66
900	0.022	0.066	0.17	0.34	0.54
1100	0.013	0.043	0.12	0.26	0.46
1300	0.008	0.028	0.082	0.20	0.38
1500	0.005	0.018	0.056	0.15	0.31
1700	0.0034	0.012	0.040	0.11	0.25
1900	0.0023	0.0082	0.028	0.081	0.20
2100	0.0015	0.0055	0.019	0.059	0.15
2300	0.001	0.0037	0.013	0.042	0.12
2500	0.0006	0.0024	0.009	0.029	0.09

(W. Tsang, May 1985)

38,26 $CH_3OH + {}^3CH_2 \rightarrow CH_3 + CH_2OH$ **(a)**
$\rightarrow CH_3 + CH_3O$ **(b)**

Reference	Conditions		Reaction rate constant,	Uncertainty
	Temp./K	[M]/molecule cm^{-3}	$k/cm^3molecule^{-1}s^{-1}$	factor
Recommended value			$k_a=5.3x10^{-23}T^{3.17}exp(-3609/T)$	3
Recommended value			$k_b=2.4x10^{-23}T^{3.1}exp(-3490/T)$	3

Comments and Recommendations

There are no data. All existing data on abstraction reactions of ${}^3CH_2$ are upper limits. For example, see ${}^3CH_2+H_2$ (26,2), ${}^3CH_2+CH_4$ (26,10), ${}^3CH_2+C_2H$ (26,11). The energetics of the processes is very similar to that for CH_3 abstraction. We therefore suggest the use of our recommended values for CH_3 attack on methanol:

$$k(CH_3OH + {}^3CH_2 \rightarrow CH_3 + CH_2OH) = 5.28x10^{-23}T^{3.17}exp(-3609/T)cm^3molecule^{-1}s^{-1}$$

$$k(CH_3OH + {}^3CH_2 \rightarrow CH_3 + CH_3O) = 2.4x10^{-23}T^{3.1}exp(-3490/T)cm^3molecule^{-1}s^{-1}$$

(W. Tsang, May 1985)

39,1 $CH_2OH + M \rightarrow H + HCHO + M$

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, $k/cm^3molecule^{-1}s^{-1}$	Uncertainty factor
Recommended value			$k_o=75T^{-2.5}exp(-17205/T)$	4
Recommended value	900-2500	N_2, 0.1-10 atm.	$1.9x10^{19}T^{-8}exp(-21645/T)$	4

Comments and Recommendations

There are no data. The values of the rate constant from the modelling of methanol pyrolysis are subject to large uncertainties. We have derived values of the rate constants using RRKM calculations and assuming a high pressure A-factor of $2.0x10^{13}$ (characteristic of radical decomposition) at 500 K and an activation energy for the reverse process of 13 kJ. The second order rate expression for hydroxymethyl decomposition is then $75T^{-2.5}exp(-17205/T)cm^3molecule^{-1}s^{-1}$. Corrections to take into account pressure effects can be found in Table A. Collision efficiencies can be found in Table B. The rate expression for decomposition at 1 atm N_2 and 900-2500 K and with a step size down of 500 cm^{-1} is: $1.9x10^{19}T^{-8}exp(-21645/T)$ $cm^3molecule^{-1}s^{-1}$. The uncertainties are factors of 4. Over this temperature range, this expression should also be valid at 0.1 and 10 atm.

Table A. $log(k/k_o)$ as a function of concentration and temperature for CH_2OH decomposition

log[M]	T/K 300	 500	 700	 900	 1100	 1300	 1500	 1700	 1900	 2100	 2300	 2500
16.5	-0.01											
17.0	-0.02	-0.02	-0.02	-0.02	-0.01	-0.01	-0.01	-0.01	-0.01	-0.01	-0.01	
17.5	-0.07	-0.05	-0.04	-0.04	-0.03	-0.03	-0.03	-0.03	-0.02	-0.02	-0.02	-0.02
18.0	-0.18	-0.15	-0.12	-0.11	-0.10	-0.09	-0.08	-0.07	-0.07	-0.05	-0.04	-0.04
18.5	-0.40	-0.34	-0.28	-0.25	-0.21	-0.18	-0.16	-0.14	-0.12	-0.11	-0.09	-0.08
19.0	-0.74	-0.62	-0.52	-0.46	-0.39	-0.34	-0.30	-0.26	-0.23	-0.20	-0.18	-0.15
19.5	-1.16	-1.10	-0.86	-0.74	-0.64	-0.56	-0.49	-0.44	-0.38	-0.33	-0.30	-0.26
20.0	-1.68	-1.43	-1.26	-1.10	-0.97	-0.85	-0.75	-0.67	-0.59	-0.52	-0.46	-0.40
20.5	-2.11	-1.91	-1.70	-1.52	-1.35	-1.20	-1.07	-0.96	-0.86	-0.77	-0.69	-0.61
21.0	-2.60	-2.40	-2.20	-1.98	-1.79	-1.61	-1.46	-1.32	-1.20	-1.08	-0.98	-0.91

Table B. Collision efficiency, βc, as a function of step size down and temperature

T/K	Step-size (cm^{-1})				
	150	300	600	1200	2400
300	0.15	0.31	0.51	0.70	0.82
500	0.07	0.18	0.35	0.55	0.73
700	0.038	0.11	0.24	0.44	0.63
900	0.023	0.068	0.17	0.34	0.55
1100	0.014	0.045	0.12	0.27	0.47
1300	0.009	0.030	0.088	0.21	0.39
1500	0.006	0.021	0.064	0.16	0.33
1700	0.004	0.015	0.047	0.13	0.28
1900	0.003	0.010	0.034	0.097	0.23
2100	0.002	0.0074	0.025	0.075	0.18
2300	0.0015	0.0053	0.018	0.057	0.15
2500	0.001	0.0038	0.014	0.043	0.12

(W. Tsang, May 1985)

39,2 $CH_2OH + H_2 \rightarrow CH_3OH + H$

	Conditions		Reaction rate constant,	Uncertainty
Reference	Temp./K	[M]/molecule cm^{-3}	$k/cm^3molecule^{-1}s^{-1}$	factor
$\log K_p = -1.8034 - 1741.76/T + 12769/T^2 - 0.3547x10^7/T^3$				
Recommended value	500-2500		$1.12x10^{-18}T^{2.02}exp(-6722/T)$	4

Comments and Recommendations

There are no data. From k values for reverse reaction (38,4) and equilibrium constant we obtain the recommended expression. Estimated uncertainty factor is 4.

(W. Tsang, May 1985)

39,3 $CH_2OH + O_2 \rightarrow HCHO + HO_2$

	Conditions		Reaction rate constant,	Uncertainty
Reference	Temp./K	[M]/molecule cm^{-3}	$k/cm^3molecule^{-1}s^{-1}$	factor
Radford (1980)	300	$1.6x10^{16}$ He, $(1.0-4.0)x10^{14}$ CH_3OH, O_2.	$2.0x10^{-12}$	2
Recommended value			$2.0x10^{-12}$	2

Comments and Recommendations

We recommend use of the reported value over all temperatures.

(W. Tsang, May 1985)

References

Radford, H. E., "The Fast Reaction of CH_2OH with O_2," Chem. Phys. Lett. 71, 195 (1980)

39,4 $H + CH_2OH \rightarrow HCHO + H_2$ (a)

$\rightarrow CH_3 + OH$ (b)

$\rightarrow CH_3OH$ (c)

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, k/cm^{3}molecule^{-1}s^{-1}	Uncertainty factor
Recommended value			$k_a=1x10^{-11}$	3
Recommended value			$k_b=1.6x10^{-10}$	2

Comments and Recommendations

There are no data. We estimate that the disproportionation reaction (a) will be somewhat faster than that for C_2H_5+H (17,3), i.e., $k_a=1.0x10^{-11}cm^3molecule^{-1}s^{-1}$ with an uncertainty of a factor of 3. The addition process (b) is the main reaction. We estimate its rate constant to be $1.6x10^{-10}cm^3molecule^{-1}s^{-1}$ with an uncertainty of a factor of 2. Calculations show that, because of the existence of an exothermic decomposition channel, the rate constant is virtually independent of pressure. The branching ratio on the basis of strong collisions can be found in Table A. Collision efficiencies, as a function of step size down and temperature, can be found in Table B. In the pressure range of 0.1, 1 and 10 atms under higher temperature conditions decomposition is the predominant process. Here we assume 500 cm^{-1} for step size down for N_2 and 1000 cm^{-1} as the step size down for CH_3OH. This is based on the general trends established in our analysis in the Introduction.

Table A. log (k_b/k_{b+c}) as a result of hydrogen addition to hydroxymethyl radical under strong collision conditions

log[M]	T/K 300	 500	 700	 900	 1100	 1300	 1500	 1700	 1900	 2100	 2300	 2500
16.0	-0.01											
16.5	-0.03	-0.01	-0.01									
17.0	-0.07	-0.04	-0.02	-0.02	-0.01							
17.5	-0.20	-0.11	-0.07	-0.04	-0.03	-0.02	-0.01	-0.01				
18.0	-0.43	-0.27	-0.15	-0.10	-0.07	-0.04	-0.02	-0.02	-0.01	-0.01	-0.01	
18.5	-0.76	-0.52	-0.35	-0.23	-0.15	-0.10	-0.07	-0.05	-0.03	-0.02	-0.02	-0.01
19.0	-1.20	-0.86	-0.60	-0.43	-0.29	-0.20	-0.14	-0.12	-0.07	-0.05	-0.04	-0.03
19.5	-1.66	-1.29	-0.95	-0.69	-0.50	-0.38	-0.27	-0.21	-0.16	-0.12	-0.10	-0.07
20.0	-2.16	-1.75	-1.36	-1.04	-0.80	-0.62	-0.48	-0.39	-0.31	-0.24	-0.20	-0.16
20.5	-2.67	-2.24	-1.82	-1.45	-1.17	-0.95	-0.77	-0.63	-0.52	-0.44	-0.36	-0.31
21.0	-3.18	-2.74	-2.30	-1.92	-1.60	-1.34	-1.17	-0.96	-0.81	-0.70	-0.61	-0.52

Table B. Collision effiency, βc, as a function of temperature and step size down

T/K	Step-size (cm^{-1})				
	150	300	600	1200	2400
300	0.15	0.32	0.52	0.70	0.83
500	0.08	0.17	0.36	0.57	0.74
700	0.043	0.12	0.26	0.46	0.65
900	0.027	0.079	0.19	0.37	0.58
1100	0.018	0.055	0.15	0.30	0.51
1300	0.012	0.038	0.11	0.24	0.43
1500	0.008	0.028	0.082	0.20	0.38
1700	0.006	0.021	0.064	0.16	0.33
1900	0.0045	0.016	0.050	0.13	0.27
2100	0.0034	0.012	0.039	0.11	0.25
2300	0.0026	0.009	0.031	0.09	0.21
2500	0.002	0.007	0.025	0.074	0.18

(W. Tsang, May 1985)

39,5 $CH_2OH + O \rightarrow HCHO + OH$

Reference	Conditions Temp./K	[M]/molecule cm^{-3}	Reaction rate constant, $k/cm^3molecule^{-1}s^{-1}$	Uncertainty factor
Recommended value			$7x10^{-11}$	2

Comments and Recommendations

There are no data. We estimate a rate constant of $7.0x10^{-11}cm^3molecule^{-1}s^{-1}$ with an uncertainty of a factor of 2.

(W. Tsang, May 1985)

39,6 $CH_2OH + OH \rightarrow H_2O + HCHO$

Reference	Conditions Temp./K	[M]/molecule cm^{-3}	Reaction rate constant, $k/cm^3molecule^{-1}s^{-1}$	Uncertainty factor
Recommended value			$4x10^{-11}$	2

Comments and Recommendations

There are no data. The estimated rate constant is $4.0x10^{-11}cm^3molecule^{-1}s^{-1}$ with an uncertainty of a factor of 2.

(W. Tsang, May 1985)

39,7 $CH_2OH + HO_2 \rightarrow H_2O_2 + HCHO$

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, k/$cm^3 molecule^{-1} s^{-1}$	Uncertainty factor
Recommended value			$2x10^{-11}$	2

Comments and Recommendations

There are no data. We recommend the rate constant $2.0x10^{-11} cm^3 molecule^{-1} s^{-1}$ with an uncertainty of a factor of 2.

(W. Tsang, May 1985)

39,8 $CH_2OH + H_2O_2 \rightarrow CH_3OH + HO_2$

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, k/$cm^3 molecule^{-1} s^{-1}$	Uncertainty factor
$\log K_p = -1.5963 + 2322.74/T - 90424.6/T^2 + 5.947x10^6/T^3$				
Recommended value			$5x10^{-15} exp(-1300/T)$	10

Comments and Recommendations

There are no data. We have used our estimated rate expression for the reverse process (38,7) and the equilibrium constant to derive the following $k_{39,8}$ value $5.0x10^{-15} exp(-1300/T) cm^3 molecule^{-1} s^{-1}$. The estimated uncertainty factor is 10.

(W. Tsang, May 1985)

39,10 $CH_2OH + CH_4 \rightarrow CH_3OH + CH_3$

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, k/$cm^3 molecule^{-1} s^{-1}$	Uncertainty factor
$\log K_p = -0.2933 - 1935.86/T - 20872/T^2 + 3.6024x10^6/T^3$				
Recommended value			$3.6x10^{-23} T^{3.14} exp(-8166/T)$	3

Comments and Recommendations

There are no data. We have used the rate expression for the reverse process, $CH_3OH + CH_3 \rightarrow CH_4 + CH_2OH$ (38,16), and the equilibrium constant to derive the rate expression

$$k(CH_2OH + CH_4 \rightarrow CH_3OH + CH_3) = 3.6\times10^{-23}T^{3.14}\exp(-8166/T)\,cm^3molecule^{-1}s^{-1}$$

The uncertainties are due mostly to possible errors in the heat of formation of CH_2OH, which we estimate, will lead to an uncertainty factor of 3 from 700 K up.
(W. Tsang, May 1985)

39,11 $CH_2OH + C_2H_6 \rightarrow C_2H_5 + CH_3OH$

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, $k/cm^3molecule^{-1}s^{-1}$	Uncertainty factor
$\log K_p = 0.02297-913.89/T-25937/T^2+1.4066\times10^6/T^3$				
Recommended value			$3.3\times10^{-22}T^{2.95}\exp(-7033/T)$	5

Comments and Recommendations

There are no data. We have used our estimated rate expression for the reverse reaction and the equilibrium constant to derive

$$k(CH_2OH + C_2H_6 \rightarrow CH_3OH + C_2H_5) = 3.3\times10^{-22}T^{2.95}\exp(-7033/T)\,cm^3molecule^{-1}s^{-1}$$

The uncertainty is a factor of 5.
(W. Tsang, May 1985)

39,12 $CH_2OH + HCHO \rightarrow CH_3OH + HCO$

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, $k/cm^3molecule^{-1}s^{-1}$	Uncertainty factor
Recommended value			$9.1\times10^{-21}T^{2.81}\exp(-2950/T)$	3

Comments and Recommendations

There are no data. In view of the constancy of the rate of alkyl radical attack on the aldehydic H at 182 C (J. A. Kerr and A. F. Trotman-Dickenson, "The Reactions of Alkyl Radicals," in 'Progress in Reaction Kinetics, Vol I,' G. Porter ed., Pergamon Press, NY, 1961, p. 107), we suggest use of our recommended rate expression for $CH_3 + H_2CO$ (12,10) leading to:

$$k(CH_2OH + HCHO \rightarrow CH_3OH + CHO) = 9.1\times10^{-21}T^{2.81}\exp(-2950/T)\,cm^3molecule^{-1}s^{-1}$$

with an uncertainty of a factor of 3.
(W. Tsang, May 1985)

39,15 $CH_2OH + HCO \rightarrow CH_3OH + CO$ (a)
$\rightarrow 2HCHO$ (b)

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, k/$cm^3molecule^{-1}s^{-1}$	Uncertainty factor
Recommended value			$k_a=2x10^{-10}$	3
Recommended value			$k_b=3x10^{-10}$	3

Comments and Recommendations

There are no data. We believe that disproportionation will be the predominant process and that it will favor the most exothermic channel. We estimate rate constants of $2.0x10^{-10}cm^3molecule^{-1}s^{-1}$ for (a) and $3.0x10^{-11}cm^3molecule^{-1}s^{-1}$ for (b). The uncertainties are a factor of 3 for each process.

(W. Tsang, May 1985)

39,16 $CH_2OH + CH_3 \rightarrow CH_3CH_2OH$ (a)
$\rightarrow CH_4 + CH_2O$ (b)

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, k/$cm^3molecule^{-1}s^{-1}$	Uncertainty factor
Recommended value			$k_a\infty=2x10^{-11}$	2
Recommended value	>900 K	1 atm N_2	$\log k_a/k_a\infty=0.202+1.755x10^{-4}T-5.61x10^{-7}T^2$	
Recommended value			$k_b=4x10^{-12}$	5

Comments and Recommendations

There are no data. The high pressure rate constant for combination should be $2.0x10^{-11}cm^3molecule^{-1}s^{-1}$ with an uncertainty of a factor of 2. Fall-off behavior on a strong collision basis can be found in Table A. Collision efficiencies as a function of temperature and step size down are given in Table B. Departure from strong collision behavior at 0.1, 1.0 and 10.0 atms for (Ar) and C_2H_5OH are as follows:

$$\log(k(Ar,\ 0.1)/k\infty) = 0.794 - 8.69x10^{-4}T - 3.794x10^{-7}T^2$$
$$\log(k(Ar,\ 1.0)/k\infty) = 0.202 + 1.755x10^{-4}T - 5.614x10^{-7}T^2$$
$$\log(k(Ar,\ 10)/k\infty) = -0.29 + 8.827x10^{-4}T - 6.307x10^{-7}T^2$$

and

$$\log(k(C_2H_5OH,\ 0.1)/k\infty) = 0.488 - 3.630x10^{-4}T - 4.395x10^{-7}T^2$$
$$\log(k(C_2H_5OH,\ 1.0)/k\infty) = -0.070 + 5.603x10^{-4}T - 5.893x10^{-7}T^2$$
$$\log(k(C_2H_5OH,\ 10)/k\infty) = -0.405 + 9.694x10^{-4}T - 5.666x10^{-7}T^2$$

where we have assumed step sizes down of 500 cm^{-1} and 1000 cm^{-1}, respectively. The results for argon should also be applicable for nitrogen.

For the disproportionation process, we estimate $k_b/k_a \sim 0.2$ with an uncertainty of a factor of 5.

Table A. Fall off behavior $\log(k/k\infty)$ for the combination of methyl and hydroxymethyl radicals assuming strong collisions

log[M]	T/K										
	500	700	900	1100	1300	1500	1700	1900	2100	2300	2500
16.0	-0.16	-0.36	-0.59	-0.87	-1.16	-1.50	-1.81	-2.11	-2.4	-2.08	-2.95
16.5	-0.08	-0.21	-0.39	-0.62	-0.87	-1.19	-1.46	-1.74	-2.01	-2.27	-2.52
17.0	-0.04	-0.11	-0.24	-0.42	-0.63	-0.90	-1.15	-1.40	-1.64	-1.88	-2.11
17.5	-0.01	-0.05	-0.13	-0.26	-0.43	-0.65	-0.86	-1.08	-1.29	-1.52	-1.73
18.0		-0.02	-0.07	-0.15	-0.27	-0.44	-0.61	-0.80	-0.99	-1.18	-1.37
18.5		-0.01	-0.03	-0.08	-0.16	-0.28	-0.41	-0.56	-0.72	-0.88	-1.05
19.0			-0.02	-0.04	-0.08	-0.16	-0.26	-0.37	-0.49	-0.62	-0.76
19.5				-0.02	-0.04	-0.08	-0.14	-0.22	-0.31	-0.41	-0.59
20.0				-0.01	-0.01	-0.04	-0.07	-0.12	-0.18	-0.24	-0.32
20.5						-0.02	-0.03	-0.06	-0.09	-0.13	-0.18
21.0							-0.01	-0.02	-0.04	-0.06	-0.09

Table B. Collision efficiency, βc, for the combination of methyl and hydroxymethyl radicals as a function of temperature and step size down

T/K	Step-size (cm^{-1})				
	150	300	600	1200	2400
300	0.15	0.31	0.51	0.69	0.83
500	0.07	0.173	0.35	0.55	0.72
700	0.045	0.124	0.27	0.47	0.66
900	0.022	0.066	0.17	0.34	0.54
1100	0.013	0.043	0.12	0.26	0.46
1300	0.008	0.028	0.082	0.20	0.38
1500	0.005	0.018	0.056	0.15	0.31
1700	0.0034	0.012	0.040	0.11	0.25
1900	0.0023	0.0082	0.028	0.081	0.20
2100	0.0015	0.0055	0.019	0.059	0.15
2300	0.001	0.0037	0.013	0.042	0.12
2500	0.0006	0.0024	0.009	0.029	0.09

(W. Tsang, May 1985)

39,17 $C_2H_5 + CH_2OH \rightarrow n\text{-}C_3H_7OH$ (a)
$\rightarrow C_2H_6 + HCHO$ (b)
$\rightarrow C_2H_4 + CH_3OH$ (c)

Reference	Conditions Temp./K	Conditions [M]/molecule cm^{-3}	Reaction rate constant, k/cm^{3}molecule^{-1}s^{-1}	Uncertainty factor
Recommended value			$k_a=2\times10^{-11}$	2
Recommended value			$k_b=4\times10^{-12}$	5
Recommended value			$k_c=4\times10^{-12}$	5

Comments and Recommendations

There are no data. The combination rate must be very close to 2×10^{-11}cm^{3}molecule^{-1}s^{-1} with an uncertainty of a factor of 2. Fall off behavior does not become important until temperatures are in excess of 1000 K. In view of the instability of ethyl and hydroxymethyl, their lifetimes at 1000 K will be short and combination cannot be an important process. We estimate the rate constants of reactions (b) and (c) to be 4×10^{-12}cm^{3}molecule^{-1}s^{-1} with an uncertainty of a factor of 5.
(W. Tsang, May 1985)

39,18 $CH_2OH + C_2H_4 \rightarrow CH_2CH_2CH_2OH$ (a)
$\rightarrow C_2H_5 + HCHO$ (b)

Reference	Conditions Temp./K	Conditions [M]/molecule cm^{-3}	Reaction rate constant, k/cm^{3}molecule^{-1}s^{-1}	Uncertainty factor
Recommended value			$k_a=8\times10^{-14}\exp(-3500/T)$ (reversed under combustion conditions)	5
Recommended value			$k_b=k_a\times(\exp(-2000/T)/(1+\exp(-2000/T)))$	5

Comments and Recommendations

There are no data. The rate constant for the addition process, as for n-propyl addition to ethylene (41,18), is estimated to be $8.0\times10^{-14}\exp(-3500/T)$cm^{3}molecule^{-1}s^{-1} since the rates of alkyl radical addition to ethylene are remarkably similar (J. A. Kerr and A. F. Trotman-Dickenson, "The Reactions of Alkyl Radicals," in 'Progress in Reaction Kinetics' Vol. I (G. Porter, ed) Pergamon Press, New York, 1961, p. 105). However, under most combustion conditions the reaction is reversible. For reaction (b), which involves a 1-4 hydrogen shift, we suggest multiplying this rate expression by the factor exp(-2000/T)(1+exp(-2000/T). The uncertainty is a factor of 5.
(W. Tsang, May 1985)

39,19 $CH_2OH + C_2H_3 \rightarrow C_2H_4 + HCHO$ (a)
$\rightarrow C_3H_5 + OH$ (b)

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, $k/cm^3 molecule^{-1} s^{-1}$	Uncertainty factor
Recommended value			$k_a=5x10^{-11}$	2.5
Recommended value			$k_b=2x10^{-11}$	2

Comments and Recommendations

There are no data. The large reaction exothermicity will lead to disproportionation products with a rate constant near collisional $5.0x10^{-11} cm^3 molecule^{-1} s^{-1}$, with an uncertainty of a factor of 2.5. The combination process (b) will lead to a hot adduct, which will decompose under combustion conditions to give C_3H_5 and OH. The rate expression is $2.0x10^{-11} cm^3 molecule^{-1} s^{-1}$ with an uncertainty of a factor of 2.

(W. Tsang, May 1985)

39,20 $CH_2OH + C_2H_2 \rightarrow C_3H_4OH$ (a)
$\rightarrow C_2H_3 + HCHO$ (b)

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, $k/cm^3 molecule^{-1} s^{-1}$	Uncertainty factor
Recommended value			$k_b=1.2x10^{-12} exp(-4531/T)$	3

Comments and Recommendations

There are no data. The rates of addition should be close to those for the addition of alkyl radicals to acetylene. The major uncertainty is the relative importance of the reverse reaction as compared to 1-4 hydrogen shift reaction (b). In view of the exothermicity of the latter, we believe it will be the major process and recommend

$$k(C_2H_2 + CH_2OH \rightarrow C_2H_3 + HCHO) = 1.2x10^{-12} exp(-4531/T) cm^3 molecule^{-1} s^{-1}.$$

This is similar to that for alkyl radical addition to acetylene. The unceratinty is a factor of 3.

(W. Tsang, May 1985)

39,21 $CH_2OH + C_2H \rightarrow C_2H_2 + HCHO$ (a)
$\rightarrow C_3H_3 + OH$ (b)

Reference	Conditions		Reaction rate constant, $k/cm^3molecule^{-1}s^{-1}$	Uncertainty factor
	Temp./K	[M]/molecule cm^{-3}		
Recommended value			$k_a=6x10^{-11}$	5
Recommended value			$k_b=2x10^{-11}$	3

Comments and Recommendations

There are no data. Taking into account the very exothermic nature of reaction (a), we estimate $k_a(CH_2OH + C_2H \rightarrow C_2H_2 + HCHO) = 6.0x10^{-11}cm^3molecule^{-1}s^{-1}$. The second decompositions channel involves combination followed by decomposition of the hot adduct. We estimate $k_b(CH_2OH + C_2H \rightarrow C_3H_3 + OH) = 2.0x10^{-11}cm^3molecule^{-1}s^{-1}$. The uncertainties are a factor of 5 and 3 respectively.

(W. Tsang, May 1985)

39,22 $CH_2OH + CH_3CO \rightarrow CH_3COCH_2OH$

Reference	Conditions		Reaction rate constant, $k/cm^3molecule^{-1}s^{-1}$	Uncertainty factor
	Temp./K	[M]/molecule cm^{-3}		
Recommended value			$2x10^{-11}$	2

Comments and Recommendations

There are no data. Combination is the main process. The rate constant is estimated to be $2.0x10^{-11}cm^3molecule^{-1}s^{-1}$, with an uncertainty of a factor of 2.

(W. Tsang, May 1985)

39,23 $CH_2OH + CH_3O_2 \rightarrow CH_3O + OH + HCHO$

Reference	Conditions		Reaction rate constant, $k/cm^3molecule^{-1}s^{-1}$	Uncertainty factor
	Temp./K	[M]/molecule cm^{-3}		
Recommended value			$2x10^{-11}$	3

Comments and Recommendations

There are no data. Under combustion conditions combination followed by rapid decomposition of the peroxide and $\cdot OCH_2OH$ will lead to the production of CH_3O, OH and HCHO. We estimate the rate constant to be $2.0x10^{-11}cm^3molecule^{-1}s^{-1}$ with an uncertainty of a factor of 3.

(W. Tsang, May 1985)

39,24 $CH_2OH + CH_3O \rightarrow CH_3OH + HCHO$

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, $k/cm^3molecule^{-1}s^{-1}$	Uncertainty factor
Recommended value			$4x10^{-11}$	2

Comments and Recommendations

There are no data. We estimate the rate constant to be $4.0x10^{-11}cm^3molecule^{-1}s^{-1}$ with an uncertainty of a factor of 2.

(W. Tsang, May 1985)

39,25 $CH_2OH + {}^1CH_2 \rightarrow CH_3CHO + H$

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, $k/cm^3molecule^{-1}s^{-1}$	Uncertainty factor
Recommended value			$3x10^{-11}$	2

Comments and Recommendations

There are no data. However, since ${}^1CH_2$ is known to insert extremely rapidly into C-H bonds, there can be no doubt that the product is an extremely hot adduct, which decomposes to acetaldehyde and a hydrogen atom. We suggest the use of a rate constant of $3.0x10^{-11}cm^3molecule^{-1}s^{-1}$, with an uncertainty factor of 2.

(W. Tsang, May 1985)

39,26 $CH_2OH + {}^3CH_2 \rightarrow C_2H_4 + OH$ (a)
$\rightarrow CH_3 + HCHO$ (b)

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, $k/cm^3molecule^{-1}s^{-1}$	Uncertainty factor
Recommended value			$k_a=4x10^{-11}$	3
Recommended value			$k_b=2.0x10^{-12}$	3

Comments and Recommendations

There are no data. One expects a fast combination, with a rate constant of ~ $4.0x10^{-11}cm^3molecule^{-1}s^{-1}$, followed by decomposition of the adduct, since the reaction is highly exothermic. The uncertainty is a factor of 3. The disproportionation reaction may be considerably slower. We estimate a rate constant of $2.0x10^{-12}cm^3molecule^{-1}s^{-1}$ with an uncertainty of a factor of 3.

(W. Tsang, May 1985)

39,38 $CH_2OH + CH_3OH \rightarrow CH_3O + CH_3OH$

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, $k/cm^3 molecule^{-1} s^{-1}$	Uncertainty factor
$\log K_p = -1.561 - 1817.2/T + 491167/T^2 - 1.044x10^7/T^3$				
Recommended value			$1.3x10^{-14} exp(-6070/T)$	10

Comments and Recommendations

There are no data. We have calculated the following recommended rate expression

$$k(CH_2OH + CH_3OH \rightarrow CH_3O + CH_3OH) = 1.3x10^{-14} exp(-6070/T) cm^3 molecule^{-1} s^{-1},$$

using the estimated reverse rate (38,14) and the equilibrium constant. The estimated uncertainty is a factor of 10.

(W. Tsang, May 1985)

39,39 $CH_2OH + CH_2OH \rightarrow HOCH_2CH_2OH$ (a)
$\rightarrow CH_3OH + HCHO$ (b)

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, $k/cm^3 molecule^{-1} s^{-1}$	Uncertainty factor
Meier, et al. (1985)			$k_{a+b}=1.5x10^{-11}$	2
Recommended value			$k_a=1.0x10^{-11}$	2
Recommended value			$k_b=5x10^{-12}$	2

Comments and Recommendations

The results of Meier et al. are in the expected range. One would expect that the greater exothermicity of the disproportionation process (b) than that for alkyl radicals would lead to a higher disproportionation to combination ratio. Therefore, we assign the value $k_b/k_a = 0.5$, with an uncertainty of a factor of 2.

(W. Tsang, May 1985)

References

Meier, V., Grotheer, H. H., Riekert, G., and Just, T., "Study of Hydroxyl Reactions with Methanol and Ethanol by Laser Induced Fluorescence," Ber. Bunsenges. Phys. Chem. 89, 325 (1985)

4. Thermodynamic Data Tables

Thermodynamic properties of CH_3OH (Species No. 38)

T/K	C_p	S	ΔH_f	ΔG_f
	J mol^{-1}K^{-1}		kJ mol^{-1}	
300	44.14	239.96	-201.17	-162.17
500	59.71	266.06	-207.86	-134.22
700	73.85	288.49	-212.71	-103.85
900	84.98	308.44	-215.98	-103.85
1100	93.60	326.45	-217.94	-40.17
1300	100.25	342.54	-219.07	-7.70
1500	108.41	357.27	-219.57	24.89

$\log K_p = -8.7463 + 12055.9/T - 402680/T^2 + 3.47379x107/T^3$

September 1985

Chen, S.S., Wilhoit, R. C., and Zwolinski, B. J.; "Thermodynamic Properties of Normal and Deuterated Methanols," J. Phys. Chem. Ref. Data, 6, 105 (1977).

Thermodynamic properties of CH_2OH (Species No. 39)

T/K	C_p	S	ΔH_f	ΔG_f
	J mol^{-1}K^{-1}		kJ mol^{-1}	
300	43.01	255.55	-17.53	-2.87
500	54.82	280.28	-21.91	8.16
700	64.79	300.38	-25.27	20.81
900	72.61	317.64	-27.72	34.32
1100	78.75	332.83	-29.41	48.29
1300	83.53	346.39	-30.56	62.51
1500	87.22	358.62	-31.39	76.90

$\log Kp = -3.89504 + 2016.76/T - 305220/T^2 + 2.87909x107/T^3$

September 1985

Frequencies are: 3300 (1), 2950 (2), 1400 (3), 1030 (1), 800 (1). 1 Free Rotor; Moment of Inertia = 1.67×10^{-40} gm cm^2 and symmetry = 1. IxIyIz = 4.45×10^{-117} gm^3 cm^6. Symmetry No. = 1. Heat of Formation at 300 K = -17.53 kJ mol^{-1} from W. Tsang, Int. J. Chem. Kin. 7, 173 (1976)

5. Transport Properties

Parameters in the Lennard-Jones Potential used to calculate transport properties pertinent to unimolecular reactions.

Substance	σ (Angstroms)	ϵ/k (K)
Argon	3.542	93.3
Helium	2.551	10.22
Krypton	3.655	178.9
Neon	2.82	32.8
Air	3.711	78.6
Methane	3.758	148.6
Carbon Monoxide	3.690	91.7
Carbon Dioxide	3.941	195.2
Acetylene	4.033	231.8
Ethylene	4.163	224.7
Ethane	4.443	215.7
Hydrogen(H2)	2.827	59.7
Nitrogen(N2)	3.798	71.1
Oxygen(O2)	3.467	106.7
Sulfur Hexafluoride	5.128	222.1
Water	2.641	804.1
Methanol	3.626	481.8
Hydroxymethyl	we used same values as for methanol	

From: Reid, R. C., Prausnitz, J. M. and Sherwood, T. K., "The Properties of Gases and Liquids" (3rd. ed.), McGraw-Hill Book Company, New York, (1977).