Chemical Kinetic Data Base for Combustion Chemistry Part V. Propene

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Chemical Kinetic Data Base for Combustion Chemistry
Part V. Propene

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This publication contains evaluated and estimated data on the kinetics of reactions involving propene and allyl radical and various small inorganic and organic species which are of importance for the proper understanding of the early stages of propene and the intermediate stages of propane and isobutane combustion and pyrolysis. It is meant to be used in conjunction with the kinetic data given in earlier publications, which is of direct pertinence to the understanding of methane, ethane, methanol, propane and isobutane pyrolysis and combustion, but which also contains a large volume of data that are applicable to the propene 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: allyl radical, combustion, data base, gas kinetics, propene, rate expressions.

Contents

1. Preface

1.1. Scope

This is the fifth of a series of papers[1,2,3,4] containing evaluated kinetic data on the gas phase reactions of organic fuels. Previously, our publications have covered the methane, ethane, methanol, propane and isobutane systems. We now expand our coverage to include the reactions involved not only in the early stages of propene combustion and pyrolysis but also in some of the subsequent stages of isobutane and propane combustion and pyrolysis. The new species that are considered are propene and allyl radical. As in our earlier work we cover all the reactions of these species with the 33 other compounds that have previously been considered as well as their self-reactions. Recommendations on the rate expressions for 57 interactions are presented. The C_3 unsaturates considered in this study represent our continuing expansion into larger and more general hydrocarbon fuels. A number of new elements are introduced into the data base. These include the presence of the allylic C–H bond and the corresponding allyl radical, the presence of two types of vinylic C–H bonds and the two different sites of unsaturation at the double bond. There are thus a large number of reaction channels that need to be considered. These data represent building blocks for future work dealing with the oxidative and pyrolytic degradation of increasingly more complex and realistic fuels. The inclusion of the reactions of propene and allyl into the data base represents our entrance into branched olefins. It should now be possible to simulate in a more complete fashion the pyrolytic aspects of combustion processes. It is the aim of this work to make available to such efforts the best available kinetic input. At the same time it is hoped that such information will serve as a ready reference to investigators of more limited aspects of the general problem. Future directions will continue to be focussed on unsaturated compounds.

Our approach is to be as inclusive as possible. Having decided on the important species that should be considered we constructed a reaction grid and examined all possible reactions of these species. In the absence of information a best possible estimate is given. Where information on a particular reaction is missing, the implication is that for all possible situations the rate constant is sufficiently small so that it can be safely ignored. The re-

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action grid containing all the reactions that have been considered can be found in Fig. 1. In all cases we give recommended rate expressions over the temperature range of 300–2500 K and the particle density range of 10^{16}–10^{21} molecules/cm^3.

1.2. Organization

The data are presented in the same fashion as in the earlier evaluations on the kinetics of methane, ethane, methanol, propane and isobutane combustion[1,2,3,4]. It is expected that the data presented here will be used in conjunction with those given in the previous publications. In the following, we provide information neccesary for the use of the information.

The numerical data are presented in the last four parts of this paper. Part 2 contains a summary of the recommended rate expressions, the estimated error limits and cthe page where a discussion can be found. Part 3 contains additional information on the individual reactions. It includes a summary of past work and the justification for the recommendations. Finally parts 4 and 5 contains relevant thermodynamic and transport property data respectively.

1.3. Guide to Summary Table

The summary table, Part 2, contains all the recommended rate expressions, the uncertainty limits and the page where a more detailed discussion can be found. In the case of unimolecular processes or the reverse we give

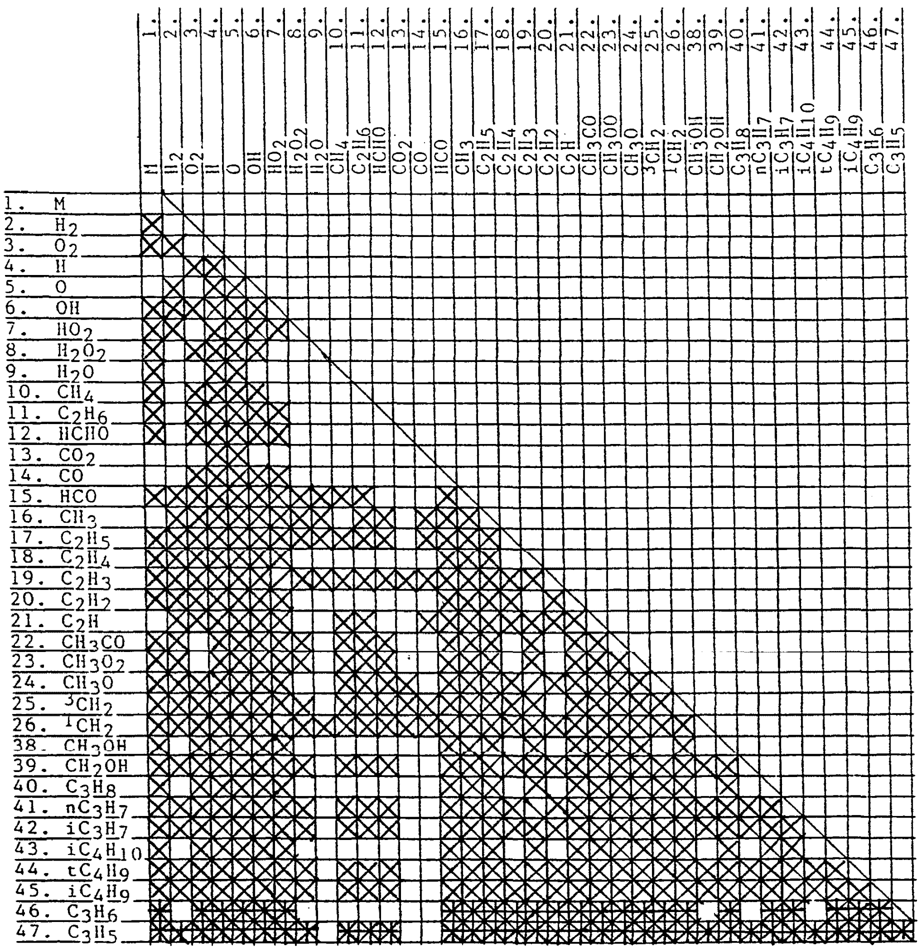

FIG. 1. Reaction Grid
X: Reactions Covered in References 1, 2, 3 and 4
+: Reactions Evaluated in Current Study

results in terms of the high pressure limit and the departure from this limit in the form of the ratio k/k_∞ for 1 atm N_2.

1.4. Guide to Chemical Kinetic Data Tables

The bulk of the work is in Part 3. It contains information on past work, our analysis of this literature and recommendations on rate expressions and uncertainty limits. We retain the numbering system that we use for the methane, propane and isobutane combustion system and to the 25 species that are labelled from 2 to 26 for the methane system, 38–39 for the methanol system, 40–42 for the propane system and 43–45 for the isobutane system we now add 46 and 47 for propene and allyl. Since pairs of these numbers form a particular reaction, we now consider reactions of these two compounds with all lower numbered species and 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 row 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 $molecule^{-2}s^{-1}$. As an aid to the user in those case where there is extensive 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[5] 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 pre-exponential factor. Unimolecular reactions and related processes are pressure and species (weak colliders) dependent as well as temperature dependent. We have applied standard RRKM[6] calculations to model the pressure and weak collider dependence. Unfortunately, the results could not be expressed in closed form. We have presented the results in the form of a rate expression for the high pressure limit and two tables from which rate constants at the reaction conditions can be obtained by interpolation. 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_∞ as a function of temperature and pressure. These are correction factors to the limiting values. 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 cast it in this form so that users can utilize their own step sizes. The values in the two 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 with 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 equivalent pressure for determining the rate constant ratios.

We illustrate the situation by carrying out fall-off calculations for allyl decomposition in the case of a dilute allyl in argon mixture at 1500 K. We begin by determining $\beta(c)$. It involves the calculation of a number of ratios. In the following, the numerator refers to the properties of the allyl-argon mixture, while the denominator refers to pure allyl itself. We have carried out these calculations to far more places than is justified by the accuracy of the data being treated. This should prevent any ambiguities and permit the reader to carry out similar calculations necessary for deriving unimolecular rate constants from the data tables.

a) Ratio of reduced masses (R); for allyl and argon this number is

$$20.26(\text{allyl-argon})/20.54(\text{allyl-allyl}) = 0.987$$

b) Ratio of collision diameters (C); for an allyl and argon mixture, this ratio is

$$[4.678(\text{allyl}) + 3.542(\text{argon})]/[4.678(\text{allyl}) \times 2] = 0.879$$

In the above and subsequent calculations we have assumed that the transport related properties of allyl radical are equal to those of propene.

c) Ratio of collision integrals (W); where we use the approximation

$$\text{collision integral} = 1/\{0.697 + 0.5185 \times \log[kT/\epsilon(\text{gas}_1\text{-gas}_2)]\}$$

and

$$\epsilon/k\ (\text{argon-allyl}) = \{[\epsilon(\text{argon-argon})/k][\epsilon(\text{allyl-allyl})/k]\}^{0.5}$$

where ϵ/k is the Lennard Jones well depth and the parenthesis refer to the two colliding gases. Since ϵ/k for allyl is 298.9 and 93.3 K for argon, then the ratio of the collision integrals is 0.839/0.943 = 0.890. The correction factor is then,

$$\beta(c) = C^2W/R^{0.5} = 0.69$$

For the allyl-argon mixture with a 600 cm^{-1} step size down the collision efficiency on a per collision basis at 1500 K is, $\beta(e) = 0.049$ see 47,1). The total collision efficiency is then

$$\beta(t) = \beta(c) \times \beta(e) = 0.049 \times 0.69 = 0.034$$

At 2 atmospheres or 10^{19} molecules/cm^3 this is equivalent to a density of 3.4×10^{17} molecules cm^{-3} for allyl as a strong collider. From Table1 of 47,1 we then find $k/k_\infty = 0.71$.

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 those 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 not as well established as for unimolecular decomposition. Fortunately, for the systems considered here pressure effects turned out to be relatively unimportant.

In the course of carrying out the earlier evaluations[1-3], 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). For strong colliders the situation is less clear, but the earlier existing data suggest step sizes down in the 1000–2000 cm^{-1} range. As an additional aid to the user and to eliminate for some cases the need to interpolate in the tables, we also include recommendations for k/k_∞ values at 0.1, 1.0 and 10 atmospheres for N_2 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

Part 4 and 5 contains information on the thermodynamic and transport properties of propene and allyl 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. There are uncertainties in the heat of formation of allyl radical. The number that we have chosen 169 kJ/mol is the average of the lower value of 163.6 kJ/mol and from of Rossi *et al.*[9] and 174.5 kJ/mol from Tsang[10,11]. The former is based on determinations of the rate constant for decomposition of 1,5 hexadiene and the combination of allyl conditions under similar conditions in very low pressure pyrolysis experiments. The latter is based on shock tube results on the decomposition of hexene-1 and a calculated combination rate constant for allyl and *n*-propyl radical assuming the geometric mean rule. The uncertainty factor is 6 kJ/mol. 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. Acknowledgements

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2. Index and Summary of Rate Expressions

No.	Reactions	Rate expressions (for second-order reactions the units are $cm^3molecule^{-1}s^{-1}$)	Uncertainty factor	Page
46,1	$C_3H_6 \rightarrow C_3H_5 + H$ (a)	$k_{a\infty} = 2.5\times10^{15}\exp(-43623/T)\ s^{-1}$	3	229
	$\rightarrow C_2H_3 + CH_3$ (b)	$k_{b\infty} = 1.1\times10^{21}T^{-1.2}\exp(-49175/T)\ s^{-1}$		
		$k_a/k_{a\infty}[1.0atm,Ar] = -0.422$		
		$+1.335\times10^{-3}T - 1.076\times10^{-6}T^2$		
		$+1.102\times10^{-10}T^3$		
		$k_b/k_b(\infty)[1.0atm,Ar] = -0.349$		
		$+1.349\times10^{-3}T - 1.408\times10^{-6}T^2$		
		$+2.132\times10^{-10}T^3$		
46,3	$C_3H_6 + O_2 \rightarrow C_3H_5 + HO_2$	$1\times10^{-10}\exp(-23950/T)$	20	230
46,4	$C_3H_6 + H \rightarrow$ (allyl)$C_3H_5 + H_2$ (a)	$k_a = 2.87\times10^{-19}(T)^{2.5}\exp(-1254/T)$	2	231
	$\rightarrow$ (propenyl)$C_3H_5 + H_2$ (b)	$k_b/k_a = 4.65\exp(-4928/T)$	3	
	$\rightarrow$ (propenyl-2)$C_3H_5 + H_2$ (c)	$k_c/k_a = 2.37$expac$(-3675/T)$	4	
	$\rightarrow n$-C_3H_7 (d)	$k_d = 1.2\times10^{-11}\exp(-1460/T)$	1.5	
	$\rightarrow C_2H_4 + CH_3$ (d')	$k_e = 1.2\times10^{-11}\exp(-655/T)$	2	
	$\rightarrow i$-C_3H_7 (e)	$\log[k(N_2,1.0)/k_\infty] = -1.119$		
		$+3.73\times10^{-3}T - 3.33\times10^{-6}T^2$		
		$+4.68\times10^{-10}T^3$		
		$\log[k_{d'}/k_{d+d'}(N_2, 1.0) = -4.737$		
		$+1.075\times10^{-2}T - 8.180\times10^{-6}T^2$		
		$+2.080\times10^{-9}T^3$		
46,5	$C_3H_6 + O \rightarrow OC_3H_6 \rightarrow CH_2CO + CH_3 + H$ (a)	$k_{a+b+c+d+e+f} = 6\times10^{-18}T^{2.15}\exp(400/T)$	1.2	233
	$\rightarrow CH_3CHCO + 2H$(b)	$k_d = 2.9\times10^{-13}T^{0.7}\exp(-2961/T)$	3	
	$\rightarrow C_2H_5 + HCO$ (c)	$k_e = 2\times10^{-13}T^{0.7}\exp(-4509/T)$	3	
	$\rightarrow C_3H_5$(allyl) $+ OH$ (d)	$k_f = 1\times10^{-13}T^{0.7}\exp(-3841/T)$	3	
	$\rightarrow CH=CHCH_3 + OH$ (e)	$k_{a+b+c} = 5.8\times10^{-17}T^{1.83}\exp(275/T)$	1.5	
	$\rightarrow CH_2=CCH_3 + OH$ (f)	$k_a/k_b = 2$	1.3	
		$k_{a+b}/k_{a+b+c} = 3.4\exp(-650/T)$	2	
46,6	$C_3H_6 + OH \rightarrow HOC_3H_6$ (a)	$k_a = 4.85\times10^{-12}\exp(504/T)$	1.15	235
	$\rightarrow C_3H_5$(allyl) $+ H_2O$ (b)	$k_b = 5.18\times10^{-18}T^2\exp(150/T)$	1.2	
	$\rightarrow C_3H_5$(propenyl) $+ H_2O$ (c)	$k_c = 3.55\times10^{-18}T^2\exp(-1398/T)$	2	
	$\rightarrow C_3H_5$(propenyl-2) $+ H_2O$ (d)	kd $= 1.8410^{-18}T^2\exp(-730/T)$		
46,7	$C_3H_6 + HO_2 \rightarrow C_3H_6O + OH$ (a)	$k_a = 1.74\times10^{-12}\exp(-7149/T)$	3	236
	$\rightarrow$ allyl$(C_3H_5) + H_2O_2$ (b)	$k_b = 1.6\times10^{-20}T^{2.6}\exp(-7000/T)$	10	
46,15	$C_3H_6 + HCO \rightarrow C_3H_5$ (allyl) $+ H_2CO$	$1.8\times10^{-17}T^{1.9}\exp(-8558/T)$	10	236
46,16	$C_3H_6 + CH_3 \rightarrow s$-$C_4H_9$ (a)	$k_a = 2.8\times10^{-13}\exp(-3726/T)$	1.4	236
	$\rightarrow i$-C_4H_9 (b)	$k_b = 1.6\times10^{-13}\exp(-4028/T)$	3.0	
	$\rightarrow$ (allyl)$C_3H_5 + CH_4$ (c)	$\log(k_b/k_{b\infty},N_2,1) = -1.2271$		
	$\rightarrow$ (1-propenyl)$C_3H_5 + CH_4$ (d)	$+5.0893\times10^{-3}T - 6.5040\times10^{-6}T^2$		
	$\rightarrow$ (2-propenyl)$C_3H_5 + CH_4$ (e)	$+2.6606\times10^{-9}T^3 - 3.7825\times10^{-13}T^4$		
		$k_c = 3.68\times10^{-24}T^{3.5}\exp(-2856/T)$	1.4	
		$k_d/k_c = 0.61\exp(-3610/T)$	6	
		$k_e/k_c = 0.38\exp(-3010/T)$	6	
46,17	$C_3H_6 + C_2H_5 \rightarrow$ (allyl) $C_3H_5 + C_2H_6$ (a)	$k_a = 3.7\times10^{-24}T^{3.5}\exp(-3340/T)$	3	239
	$\rightarrow C_2H_4 + nC_3H_7$ (b)	$k_{total} = 1.7\times10^{-13}\exp(-3625/T)$	2	
		$k_b/k_{total} = 1/(1+0.66\exp(1000/T)$	3	
46,18	$C_3H_6 + C_2H_4 \rightarrow$ 1-pentene (a)	$k_a = 5.3\times10^{-21}T^{2.2}\exp(-17151/T)$	1.5	240
	$\rightarrow C_3H_5$(allyl) $+ C_2H_5$ (b)	$k_b = 9.6\times10^{-11}\exp(-25958/T)$	3	
	$\rightarrow n$-$C_3H_7 + C_2H_3$ (c)	$k_c = 1\times10^{-10}\exp(-37966/T)$	3	
	$\rightarrow i$-$C_3H_7 + C_2H_3$ (d)	$k_d = 1.2\times10^{-8}T^{-0.65}\exp(-37051/T)$	3	
46,19	$C_3H_6 + C_2H_3 \rightarrow C_3H_5$(allyl) $+ C_2H_4$ (a)	$k_a = 3.68\times10^{-24}T^{3.5}\exp(-2356/T)$	6	240
	$\rightarrow C_3H_5$(1-propenyl) $+ C_2H_4$ (b)	$k_b/k_a = 0.61\exp(-3110/T)$	6	
	$\rightarrow C_3H_5$(2-propenyl-2) $+ C_2H_4$(c)	$k_c/k_a = 0.38\exp(-2510/T)$	6	
	$\rightarrow$ 1,3-$C_4H_6 + CH_3$(d)	$k_d = 1.2\times10^{-12}\exp(-2520/T)$	3	
	$\rightarrow$ 1,3-$C_5H_{10} + H$(e)	$k_e = 1.2\times10^{-12}\exp(-3240/T)$	3	

2. Index and Summary of Rate Expressions – Continued

No.	Reactions	Rate expressions (for second-order reactions the units are cm^{3}molecule^{-1}s^{-1})	Uncertainty factor	Page
46,20	$C_3H_6 + C_2H_2 \rightarrow C_3H_5 + C_2H_3$	$6.7\times10^{-11}\exp(-23560/T)$	2.5	241
46,21	$C_3H_6 + C_2H \rightarrow$ 1-butyne + H (a)	$k_a = 2\times10^{-11}$	2.5	241
	$\rightarrow$ 1-propyne + CH_3 (b)	$k_b = 2\times10^{-11}$	2.5	
	$\rightarrow C_3H_5$ (allyl) + C_2H_2 (c)	$k_c = 6\times10^{-12}$	3	
	$\rightarrow$ 1-propenyl + C_2H_2 (d)	$k_d = 2\times10^{-12}$	5	
	$\rightarrow$ 2-propenyl + C_2H_2 (e)	$k_e = 2\times10^{-12}$	5	
46,22	$C_3H_6 + CH_3OO \rightarrow C_3H_6O + CH_3O$ (a)	$k_a = 6.6\times10^{-13}\exp(-5900/T)$	4	242
	$\rightarrow C_3H_5 + CH_3OOH$ (b)	$k_b = 3.3\times10^{-12}\exp(-8581/T)$	10	
46,23	$C_3H_6 + CH_3CO \rightarrow C_3H_5 + CH_3CHO$	$8.8\times10^{-18}T^2\exp(-8173/T)$	10	242
46,24	$C_3H_6 + CH_3O \rightarrow C_3H_5 + CH_3OH$	$90T^{2.95}\exp(-6032/T)$	10	242
46,25	$C_3H_6 + {}^1CH_2 \rightarrow {}^3CH_2 + C_3H_6$ (a)	$k_a = 5\times10^{-11}$	1.5	243
	$\rightarrow C_3H_5 + CH_3$ (b)	$k_b = 8.7\times10^{-11}$	5	
	$\rightarrow$ 2-C_4H_8 (c)	$k_c = 7.2\times10^{-11}$	5	
	$\rightarrow$ i-C_4H_8 (d)	$k_d = 0.9\times10^{-11}$	5	
46,26	$C_3H_6 + {}^3CH_2 \rightarrow {}^1CH_2 + C_3H_6$ (a)	$k_a = 2\times10^{-11}\exp(-4480/T)$	1.5	244
	$\rightarrow C_3H_5 + CH_3$ (b)	$k_b = 1.2\times10^{-12}\exp(-3116/T)$	3	
	$\rightarrow C_3H_5 + CH_3$ (c)	$k_c = 2.7\times10^{-12}\exp(-2660/T)$	5	
	$\rightarrow$ 2-C_4H_8 (d)	$k_d = 2.7\times10^{-12}\exp(-2660/T)$	5	
46,39	$C_3H_6 + CH_2OH \rightarrow C_3H_5 + CH_3OH$ (a)	$k_a = 1\times10^{-22}T^{2.95}\exp(-6033/T)$	10	245
	$\rightarrow$ n-C_3H_7 + HCHO (b)	$k_b = 2\times10^{-14}\exp(-3273/T)\times \exp(-2500/T)/(1+\exp(-2500/T))]$	10	
	$\rightarrow$ i-C_3H_7 + HCHO ()	$k_c = 2\times10^{-14}\exp(-4000/T)\times [\exp(-1700/T)/(1+\exp(-1700/T))]$	10	
46,41	$C_3H_6 + n$-$C_3H_7 \rightarrow C_3H_5$(allyl) + C_3H_8 (a)	$k_a = 3.7\times10^{-24}T^{3.5}\exp(-3340/T)$	3	246
	$\rightarrow$ 2-C_2H_4 + C_2H_5 (b)	$k_{b+c+d} = 1.7\times10^{-13}\exp(-3625/T)$	3	
	$\rightarrow$ 1-C_4H_8 + C_2H_5 (c)	$k_b/k_{b+c+d} = 1/(1+1.33\exp(1000/T)$	3	
	$\rightarrow$ 1-C_5H_{10} + CH_3 (d)	$k_c+{}_d/k_{b+c+d} = 1/(2+1.5\exp(-1000/T)$	3	
		$k_c/k_d = \exp(+1000/T)$	3	
46,42	$C_3H_6 + i$-$C_3H_7 \rightarrow C_3H_5 + C3H_8$ (a)	$k_a = 1.1\times10^{-25}T^4\exp(-4059/T)$	3	246
	$\rightarrow C_3H_6 + n$-C_3H_7 (b)	$k_{b+c+d} = 2.2\times10^{-14}\exp(-3110/T)$	3	
	$\rightarrow C_2H_4 + i$-C_4H_9 (c)	$k_b/k_{b+c+d} = 1.13\exp(-1437/T)$	>3	
	$\rightarrow$ i-$C_4H_8 + C_2H_5$ (d)	$k_c/k_{b+c+d} = 0.57\exp(-1437/T)$	>3	
		$k_d/k_{b+c+d} = 0.18\exp(562/T)$	>3	
46,44	$C_3H_6 + t$-$C_4H_9 \rightarrow C_3H_5$(allyl) + i-C_4H_{10} (a)	$k_a = 5\times10^{-29}T^{4.9}\exp(-4208/T)$	6	247
	$\rightarrow C_2H_4 + i$-$C_4H_8 + CH_3$ (b)	$k_{\mathrm{terminal}} = 5.1\times10^{-15}\exp(-2962/T)$	10	
		$k_b/k_{\mathrm{terminal}} < 1/(1+0.16\exp(1000/T))$		
46,45	$C_3H_6 + i$-$C_4H_9 \rightarrow C_3H_5$(allyl) + i-C_4H_{10} (a)	$k_a = 3.7\times10^{-24}T^{3.5}\exp(-3340/T)$	3	248
	$\rightarrow$ i-C_4H_8 + n-C_3H_7 (b)	$k_{\mathrm{terminal}} = 1.7\times10^{-13}\exp(-3625/T)$	3	
	$\rightarrow C_3H_6 + C_2H_4 + C_2H_5$ (c)	$k_b = k_{\mathrm{terminal}}/\mathrm{total}$	5	
	$\rightarrow$ 2-C_2H_4 + i-C_3H_7 (d)	$k_c = k_{\mathrm{terminal}}\times6\exp(-2000/\mathrm{total}$	5	
	$\rightarrow$ 3-methylbutene-1 + C_2H_5 (e)	$k_d = k_{\mathrm{terminal}}\times3\exp(-2000)/\mathrm{total}$	5	
	$\rightarrow C_4H_8$–1 + i-C_3H_7 (f)	$k_e = k_{\mathrm{terminal}}\times2\exp(-1000/T)/\mathrm{total}$	5	
		$k_f = k_{\mathrm{terminal}}\times2\exp(-1000/T)/\mathrm{total}$	5	
		where total $= 1+6\exp(-1000/T) + 9\exp(-2000/T)$		
46,46	$C_3H_6 + C_3H_6 \rightarrow$ 1-hexene (a)	$k_a = 2.1\times10^{-22}T^{2.5}\exp(-26463/T)$	2.5	248
	$\rightarrow$ 4-methylpentene-1 (b)	$k_b = 2.8\times10^{-21}T^{2.1}\exp(-18114/T)$	1.5	
	$\rightarrow C_3H_5$ + n-C_3H_7 (c)	$k_c = 4.2\times10^{-10}\exp(-27767/T)$	2.5	
	$\rightarrow C_3H_5$ + i-C_3H_7 (d)	$k_d = 8.1\times10^{-11}\exp(-26323/T)$	2.5	
47,1	$C_3H_5 \rightarrow C_3H_4 + H$	$1.4\times10^{13}\exp(-30192/T)$	4 at 500	249
		$\log(k(N_2,1.0)/k_\infty) = -0.8103+2.0134\times10^{-3}T - 1.4016\times10^{-6}T^2+2.0671\times10^{-10}T^3$	2 at 1500	

2. Index and Summary of Rate Expressions — Continued

No.	Reactions	Rate expressions (for second-order reactions the units are cm³molecule⁻¹s⁻¹)	Uncertainty factor	Page
47,2	C_3H_5(allyl) + H_2 → C_3H_6 + H	$1.8\times10^{-19}\ T^{2.38}\exp(-9557/T)$	5 at 300 2 at 1100	250
47,3	C_3H_5(allyl) + O_2 → $C_3H_5O_2$ (a) → C_3H_4 + HO_2 (b)	 $k_b<2\times10^{-12}\exp(-6820/T)$		251
47,4	C_3H_5 + H → C_3H_6 (a) → C_2H_3 + CH_3 (b) → C_3H_4 + H_2 (c)	$k_a+k_b=3.3\times10^{-10}$ $\log(k_b/k_{b+a},N_2,1.0)$ = $-13.6030+2.0026\times10^{-2}T$ $-9.9065\times10^{-6}T^2+1.6333\times10^{-9}T^3$ $k_c=3\times10^{-11}$	3 3	252
47,5	C_3H_5(allyl) + O → C_2H_3CHO + H	1.0×10^{-10}	2.5	253
47,6	C_3H_5(allyl) + OH → C_3H_4 + H_2O (a) → C_3H_5OH (b) → C_2H_3CHO + 2H (c)	$k_a=1\times10^{-11}$ $k_{b+c}=2.5\times10^{-11}$ $\log(k_{b+c}/k_{b+c\infty},N_2,1.0)$ = $-0.6720+1.9954\times10^{-3}T$ $-1.6251\times10^{-6}T^2+3.2547\times10^{-10}T^3$ $\log(k_c/k_{b+c},N_2,1.0)$ = $-13.2116+1.6774\times10^{-2}T$ $-7.4344\times10^{-6}T^2+1.1378\times10^{-9}T^3$	3 2	253
47,7	C_3H_5(allyl) + HO_2 → OH + C_3H_5O → C_2H_3CHO(acrolein) + H	1.6×10^{-11}	3	255
47,8	C_3H_5(allyl) + H_2O_2 → C_3H_6 + HO_2	$6.5\times10^{-19}T^{2.05}\exp(-6833/T)$	5	255
47,10	C_3H_5(allyl) + CH_4 → C_3H_6 + CH_3	$6.6\times10^{-23}T^{3.4}\exp(-11669/T)$	3	256
47,11	C_3H_5(allyl) + C_2H_6 → C_3H_6 + C_2H_5	$3.9\times10^{-22}T^{3.3}\exp(-9986/T)$	4	256
47,12	C_3H_5 (allyl) + HCHO → C_3H_6 + CHO	$2.1\times10^{-16}T^{1.8}\exp(-9154/T)$	10	256
47,15	C_3H_5(allyl) + HCO → C_3H_6 + CO (a) → C_3H_5CHO (b)	$k_a = 1\times10^{-10}$ $k_b = 2\times10^{-11}$	5 2	257
47,16	C_3H_5(allyl) + CH_3 → CH_4 + C_3H_4(allene) (a) → C_4H_8 (1-butene)(b)	$k_a=0.05\times10^{-10}T^{-0.32}\exp(66/T)$ $k_{b\infty}=1.69\times10^{-10}T^{-0.32}\exp(66/T)$ $\log k_a/k_{a,\infty}(N_2,1.0) = -1.4674$ $+3.5845\times10^{-3}T-2.4575\times10^{-6}T^2$ $+3.7803\times10^{-10}T^3$	3 1.5	257
47,17	C_3H_5(allyl) + C_2H_5 → C_3H_4(allyl) + C_2H_6 (a) → C_3H_6 + C_2H_4 (b) → 1-C_5H_{10} (c) → C_3H_6 + C_2H_4 (d)	$k_{c+d}=3.3\times10^{-11}\exp(66/T)$ $k_a=1.6\times10^{-12}\exp(66/T)$ $k_b=4.3\times10^{-12}\exp(66/T)$ $\log(k_{c+d}(N_2,1.0)/k_{c+d\infty})$ = $-1.8581+4.7581\times10^{-3}T$ $-3.5095\times10^{-6}T^2+6.3896\times10^{-10}T^3$ $\log(k_c/(k_{c+d}),N_2,1)$ = $+0.1125-3.3027\times10^{-4}T$ $+3.1937\times10^{-7}T^2-1.0478\times10^{-10}T^3$	1.5 2 2	259
47,18	C_3H_5(allyl) + C_2H_4 → cyclopentene + H	$1\times10^{-14}\exp(-5776/T)$	10	261
47,19	C_3H_5 + C_2H_3 → 1,4 C_5H_8 (a) → C_5H_6 + 2H (b) → C_3H_6 + C_2H_2 (c) → C_3H_4 + C_2H_4 (d)	$k_{a+b}=8\times10^{-11}$ $k_c=8\times10^{-12}$ $k_d=4\times10^{-12}$ $\log(k_{a+b}/k_{a+b\infty},N_2,1.0)$ = $-5.5048+1.1143\times10^{-2}T$ $-7.0231\times10^{-6}T^2+1.2985\times10^{-9}T^3$ $\log(k_b/k_{a+b},N_2,1.0)=-17.9735$ $+2.6305\times10^{-2}T-1.6929\times10^{-5}T^2$ $+5.5107\times10^{-9}T^3-7.1958\times10^{-13}T^4$	2 3 3	261
47,20	C_3H_5(allyl) + C_2H_2 → C_5H_7 (a) → cyclopentadiene + H (b)	$k_a=5.3\times10^{-14}\exp(-3500/T)$ $k_b=6.6\times10^{-10}\exp(-12526/T)$	10 3	263

2. Index and Summary of Rate Expressions – Continued

No.	Reactions	Rate expressions (for second-order reactions the units are $cm^3molecule^{-1}s^{-1}$)	Uncertainty factor	Page
47,21	C_3H_5(allyl) + $C_2H \rightarrow C_5H_6$ (a)	$k_{a+b+c} = 8 \times 10^{-11}$	3	264
	$\rightarrow C_2H_3 + C_3H_3$ (b)	$k_b/k_c = 20$	3	
	$\rightarrow C_5H_5 + H$ (c)	$\log[(k_{b+c})/(k_{a+b+c}),N_2,1.0]$		
	$\rightarrow C_3H_4 + C_2H_2$ (d)	$= -6.4434 + 1.0743 \times 10^{-2}T$		
		$-5.8204 \times 10^{-6}T^2 + 1.0250 \times 10^{-9}T^3$		
		$k_d/k_{a+b+c} = 0.15$	3	
47,22	C_3H_5(allyl) + $CH_3CO \rightarrow C_3H_5COCH_3$	3×10^{-11}	2	265
47,23	C_3H_5(allyl) + $CH_3OO \rightarrow C_2H_3CHO + H + CH_3O$	1.6×10^{-11}	2.5	265
47,24	C_3H_5(allyl) + $CH_3O \rightarrow C_3H_6 + CH_2O$	5×10^{-11}	3	266
47,25	C_3H_5(allyl) + $^1CH_2 \rightarrow C_4H_7 \rightarrow 1,3C_4H_6 + H$(a)	4×10^{-10}	3	266
	$\rightarrow C_2H_3 + C_2H_4$(b)	$k_a/k_b = 5$	3	
47,26	C_3H_5(allyl) + $^3CH_2 \rightarrow C_4H_7 \rightarrow 1,3C_4H_6 + H$(a)	5×10^{-11}	2.5	266
	$\rightarrow C_2H_3 + C_2H_4$ (b) $k_a/k_b = 4$	3		
47,38	C_3H_5(allyl) + $CH_3OH \rightarrow C_3H_6 + CH_2OH$	$2.9 \times 10^{-21}T^{2.9}\exp(-10294/T)$	10	267
47,39	C_3H_5(allyl) + $CH_2OH \rightarrow C_3H_6 + CH_2O$	3×10^{-11}	2.5	267
47,40	C_3H_5(allyl) + $C_3H_8 \rightarrow C_3H_6 + n\text{-}C_3H_7$ (a)	$k_a = 3.9 \times 10^{-22}(T)^{3.3}\exp(-9986/T)$	5	267
	$\rightarrow C_3H_6 + i\text{-}C_3H_7$ (b)	$k_b = 1.3 \times 10^{-22}(T)^{3.3}\exp(-9144/T)$	5	
47,41	C_3H_5(allyl) + $n\text{-}C_3H_7 \rightarrow 2\text{-}C_3H_6$ (a)	$k_a = 2.4 \times 10^{-12}\exp(66/T)$	3	268
	$\rightarrow C_3H_4 + C_3H_8$ (b)	$k_b = 1.2 \times 10^{-12}\exp(66/T)$	3	
	$\rightarrow 1\text{-}C_6H_{12}$ (c)	$k_c = 3.4 \times 10^{-11}\exp(66/T)$	2	
47,42	C_3H_5(allyl) + $i\text{-}C_3H_7 \rightarrow 2\text{-}C_3H_6$ (a)	$k_c = 1.9 \times 10^{-10}(T)^{-0.35}\exp(66/T)$	1.5	268
	$\rightarrow C_3H_4 + C_3H_8$ (b)	$k_a = 3.8 \times 10^{-11}(T)^{-0.35}\exp(66/T)$	3	
	$\rightarrow$ 4-methylpentene-1(c)	$k_b = 7.6 \times 10^{-12}(T)^{-0.35}\exp(66/T)$	3	
47,43	C_3H_5(allyl) + $i\text{-}C_4H_{10} \rightarrow C_3H_6 + i\text{-}C_4H_9$(a)	$k_a = 5.9 \times 10^{-22}(T)^{3.3}\exp(-9986/T)$	5	269
	$\rightarrow C_3H_6 + t\text{-}C_4H_9$(b)	$k_b = 0.7 \times 10^{-22}(T)^{3.3}\exp(-8640/T)$	5	
47,44	C_3H_5(allyl) + $t\text{-}C_4H_9 \rightarrow C_3H_6 + i\text{-}C_4H_8$ ()	$k_c = k_c = 1.2 \times 10^{-9}T^{-0.75}\exp(66/T)$	1.5	269
	$\rightarrow C_3H_4 + i\text{-}C_4H_{10}$ (b)	$k_b = 4.8 \times 10^{-11}T^{-0.75}\exp(66/T)$	3	
	$\rightarrow$ 4,4-dimethylpentene-1(c)	$k_a = 0.72 \times 10^{-9}T^{-0.75}\exp(66/T)$	3	
47,45	C_3H_5(allyl) + $i\text{-}C_4H_9 \rightarrow C_3H_6 + i\text{-}C_4H_8$ (a)	$k_c = 3.4 \times 10^{-11}\exp(66/T)$	2	270
	$\rightarrow C_3H_4 + i\text{-}C_4H_{10}$ (b)	$k_b = 1.3 \times 10^{-12}\exp(66/T)$	3	
	$\rightarrow$ 5-methylhexene-1 (c)	$k_a = 1.3 \times 10^{-12}\exp(66/T)$	3	
47,46	C_3H_5(allyl) + $C_3H_6 \rightarrow$ methylcyclopentene + H	$1 \times 10^{-14}\exp(-5776/T)$	10	270
47,47	2-C_3H_5(allyl) $\rightarrow C_6H_{10}$(1,5 hexadiene) (a)	$k_{a\infty} = 1.7 \times 10^{-11}\exp(132/T)$	2	271
		$\log [k_a/k_{a\infty},N_2,0.1) =$		
		$-1.309 + 3.052 \times 10^{-3}T - 2.075 \times 10^{-6}T^2$		
		$+3.347 \times 10^{-10}T^3$		
		$k_b = 1.4 \times 10^{-13}\exp(132/T)$	2.5	

3. Chemical Kinetics Data Tables

46,1 $C_3H_6 \rightarrow C_3H_5 + H$ (a)
$\rightarrow C_2H_3 + CH_3$ (b)

Reaction	Conditions T range/K	 [M] range/cm³	Reaction constant (for second-order reactions the units are cm³molecule⁻¹s⁻¹)	Uncertainty
Rao and Skinner(1989)	1500–1800	10 ppm CD_2CHCH_3; 20 ppm CH_2CDCH_3; 10 ppm CH_2CHCD_3; $1.9–14\times10^{18}$ Ar ARAS detection of H and D behind incident and reflected shocks.	$k_a(1600,0.42\text{atm})=100\ s^{-1}$ $k_b(1600,0.42\text{atm})=200\ s^{-1}$ $k_a(1600,2.8\text{atm})=260\ s^{-1}$ $k_b(1600,2.8\text{atm})=350\ s^{-1}$	2.5
Kiefer *et al.* (1982)	1650–2230	2–10% C_3H_6 6 13.2×10^{18} Kr laser schlieren behind shock waves	$k_{a+b}=8.9\times10^{51}T^{-15.7}\exp(-60420/T)$	2
Burcat (1975)	1160–1670	0.4–1.6% C_3H_6 $7–42\times10^{18}$ Ar in single pulse shock tube experiments	$k_{a+b}=10^{13}\exp(-37261/T)$	3
Chappell and Shaw (1968)	1100–1650	0.87% C_3H_6 7×10^{19} Ar in single pulse shock tube experiments	$k_{a+b}=1.3\times10^{16}\exp(-43200/T)\ s^{-1}$	3
Szwarc (1949)	953–1143	8×10^{16} C_3H_6 in flow experiments	$k_a+_b=1.1\times10^{13}\exp(-36250/T)\ s^{-1}$	3
Recommendations			$k_{a\infty}=2.5\times10^{15}\exp(-43623/T)\ s^{-1}$ $k_{b\infty}=1.1\times10^{21}T^{-1.2}$ $\exp(-49175/T)s^{-1}$	3
			$k_a/k_{a\infty}[1.0\text{atm,Ar}]=-0.422$ $+1.335\times10^{-3}T-1.076\times10^{-6}T^2$ $+1.102\times10^{-10}T^3$ $k_b/k_{b\infty}[1.0\text{atm,Ar}]=-0.349$ $+1.349\times10^{-3}T-1.408\times10^{-6}T^2$ $+2.132\times10^{-10}T^3$	2

Comments

The existing data show considerable scatter. Our recommendations for the limiting high pressure rate expressions are based on a recombination rate constant for allyl + H of 3.3×10^{-10} cm³molecule⁻¹s⁻¹ and 1.2×10^{-10} cm³molecule⁻¹s⁻¹ for vinyl + CH_3 and the thermodynamics used in these evaluations. The rate constant for the latter was derived from the results of Fahr, A.,and Laufer, A. H., (J. Phys. Chem, 1990, **94**, 726) on vinyl combination and the geometric mean rule. This leads to;

$$k_{a\infty}=2.5\times10^{15}\exp(-44076/T)\ s^{-1}$$

$$k_{b\infty}=1.1\times10^{21}T^{-1.2}\exp(-49175/T)\ s^{-1}$$

Assumming the following relation for the step size down; $\Delta\ E_{\text{down}}=120(T/300)$ cm^{-1} for N_2 and Ar, we find,

$$k_a/k_{a\infty}[0.1\text{atm},N_2] = -0.544+1.931\times10^{-3}T-1.849\times10^{-6}T^2+2.909\times10^{-10}T^3$$

$$k_b/k_{b\infty}[0.1\text{atm},N_2] = -0.1155+8.842\times10^{-4}T-1.591\times10^{-6}T^2+2.874\times10^{-10}T^3$$

$$k_a/k_{a\infty}[1.0\text{atm},N_2] = -0.422\ +1.335\times10^{-3}T-1.076\times10^{-6}T^2+1.102\times10^{-10}T^3$$

$$k_b/k_{b\infty}[1.0\text{atm},N_2] = -0.349+1.349\times10^{-3}T-1.408\times10^{-6}T^2+2.132\times10^{-10}T^3$$

$$k_a/k_{a\infty}[10\text{atm},N_2] = -0.181+4.796\times10^{-4}T-2.411\times10^{-7}T^2+6.303\times10^{-11}T^3$$

$$k_b/k_{b\infty}[10\text{atm},N_2] = -0.286+8.993\times10^{-4}T-7.065\times10^{-7}T^2+4.945\times10^{-11}T^3$$

Comparison of the recommendations and experimental results can be seen in Fig. 1. The recommendations are within a factor of 2 of the laser schlieren work in terms of total rate constants and and a factor of 3 higher than the total rate constants from the ARAS studies. The lower temperature studies are bracketed by the experimental results of Chappell and Shaw and Szwarc and that of Burcat. For the first two studies no provisions were made for radical induced decomposition processes. The results are compatible with short chain lengths. This is expected since propene is a chemical inhibitor by virtue of the stability of allyl radicals. The latter was derived on the basis of a modeling study and it would appear that the importance of some of the chain processes are overestimated.

The only results on the branching ratios for the two channels are from the ARAS studies. The recommendations yield ratios which are in fair agreement. From the discussion by Rao and Skinner the possibility of distortions from isotopic scrambling cannot be ruled out.

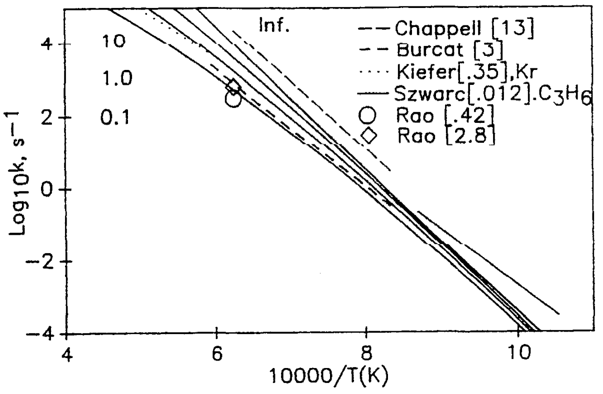

FIG. 1. Total rate constant as a function of temperature. The four solid lines represent our recommendations. The numbers are the reaction pressures in atm.

Due to the contributions from the two channels it is not possible to express the results in terms of the universal tables as in single channel decomposition. We recommend the use of the k/k_∞ values in combustion modeling. Note that for these multi-channel processes the branching ratio is particularly sensitive to the step sizes chosen. This is the reason for putting in the temperature dependent step size down. It does lead to a value near 600 cm^{-1} at 1500 K. It is the value that has been used in other calculations of pressure dependent effects. The actual evidence for the temperature dependence of the step size down is very sparse.

The overall uncertainty is estimated to be a factor of 3 in total rate constants and a factor of 2 in the branching ratios for the two processes. It should be noted that the stability to thermal decomposition for propene means that except where it is used as a fuel other processes will be more influential in effecting destruction.

References

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March 1990

46,3 $C_3H_6 + O_2 \rightarrow C_3H_5 + HO_2$

	Conditions		Reaction rate constant	Uncertainty
Reference	T range/K	[M] range/cm^3	$k/cm^3 molecule^{-1} s^{-1}$	
Recommendations			$1 \times 10^{-10} \exp(-23950/T)$	20

Comments

There are no measurements on the mechanisms or rates for this reaction. The available data on the abstractionof an allylic hydrogen indicates that the rates are comparable to that for a secondary hydrogen. Thus from our recommendation of O_2 attack on the secondary hydrogen in propane we arrive at $1 \times 10^{-10} \exp(-23950/T)$ cm^3 $molecule^{-1} s^{-1}$ with an uncertainty of a factor of 20.

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September, 1988

46,4 $C_3H_6 + H \rightarrow$ (allyl)$C_3H_5 + H_2$ (a)
$\rightarrow$ (propenyl)$C_3H_5 + H_2$ (b)
$\rightarrow$ (propenyl-2)$C_3H_5 + H_2$ (c)
$\rightarrow n\text{-}C_3H_7$ (d)
$\rightarrow C_2H_4 + CH_3$ (d′)
$\rightarrow i\text{-}C_3H_7$ (e)

	Conditions		Reaction rate constant	Uncertainty
Reference	T range/K	[M] range/cm^3	k/cm^{3}molecule^{-1}s^{-1}	
Harris and Pitts, 1982	298–445	C_3H_6 and CH_4 in 1.3×10^{18} Ar. H-atoms from resonance absorption	$k_{d+e}=2.2\times10^{-11}\exp(-785/T)$	1.1
Kerr and Parsonage, 1972 (review)	300–800		$k_d=1.2\times10^{-11}\exp(-1460/T)$ $k_e=1.2\times10^{-11}\exp(\;604/T)$	2 1.5
Recommendations			$k_a=2.87\times10^{-19}(T)^{2.5}\exp(-1254/T)$ $k_b/k_a=4.65\exp(-4928/T)$ $k_c/k_a=2.37\exp(-3675/T)$ $k_{d\infty}=2.2\times10^{-11}\exp(-1641/T)$ $k_{e\infty}=2.2\times10^{-11}\exp(-785/T)$ $\log[k(N_2,1.0)/k_\infty]=-1.119+3.73\times10^{-3}T-3.33\times10^{-6}T^2+4.68\times10^{-10}T^3$ $\log[k_{d'}/k_{d+d'}(N_2,1.0)=-4.737+1.075\times10^{-2}T-8.180\times10^{-6}T^2+2.080\times10^{-9}T^3$	2 3 4 2 1.5

Comments

All of the low temperature experimental measurements are for terminal addition. Since this reaction is reversed at combustion temperatures it is not of major importance for the present purposes. There are no measurments on the rate expressions for the abstraction processes. For abstraction of allylic hydrogens our recommendation is based on the rate expression for abstraction of an allylic hydrogen from isobutene (Tsang and Walker, 22nd Symposium on Combustion (International), The Combustion Institute, Pittsburgh Pa., 1988, 1015) and scaled for all temperatures using a $T^{2.5}$ dependence in the prexponential factor. For k_b we recommend $0.5\times k(H+C_2H_4 \rightarrow C_2H_3 + H_2)$(18,4).

For k_c our recommendation is based on the assumption that the effect of methyl substitution is the same in olefins as in alkanes. This leads to the following rate expressions;

$$k_a = 2.87\times10^{-19}(T)^{2.5}\exp(-1254/T)\ \text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$$
$$k_b/k_a = 4.65\exp(-4928/T)\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$$
$$k_c/k_a = 2.37\exp(-3675/T)\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$$

The uncertainties are factors of 2, 3, and 4 for the three processes respectively at temperatures in excess of 900 K.

At low temperatures the primary process is addition to the terminal position. We recommend the results of Harris and Pitts which are essentially the same at room temperature as that of Kerr and Parsonage on the limiting high pressure rate expressions for terminal addition, but cover a slightly higher temperature range. Thus

$$k_e = 2.2\times10^{-11}\exp(-785/T)\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$$

with an uncertainty of a factor of 1.5. For non-terminal addition we make use of the data of Falconer and Sauder (Int. J. Chem. Kin., 3, 395, 1971) which gives the ratio of terminal to non-terminal addition at room temperature as approximately 0.05. Assuming that this is all due to changes in the activation energy leads to

$$k_e = 1.2\times10^{-11}\exp(-1641/T)\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$$

with an uncertainty of a factor of 3. A similar treatment of the data for terminal to non-terminal addition to isobutene yielded fairly satisfactory results (Tsang and Walker, 22nd Symposium on Combustion (International), The Combustion Institute, Pittsburgh Pa., 1988, 1015). A plot of our recommendations can be found in Fig. 1.

These plots are somewhat deceptive due to the fact that isopropyl radical decomposition is sufficiently fast so that over most high temperature ranges the addition reaction is reversed. Isopropyl radicals decomposition is already in our data base (42,1). Thus the reversibility of this reaction is automatically taken care of. We summarize in Table 1 the results of RRKM calculations on the pressure and temperature dependence of this process assumming strong collisions. Collision efficiencies for various step sizes down are given in Table 2.

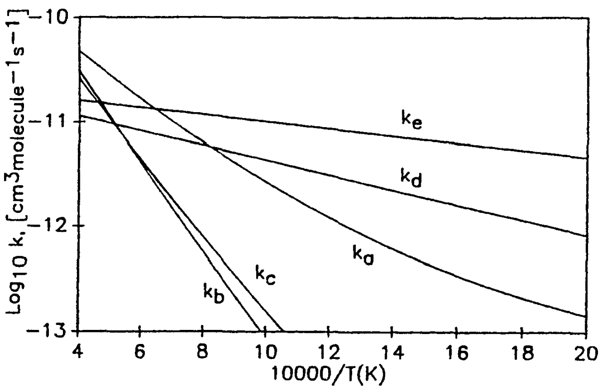

FIG. 1. Recommended rate constants for hydrogen atom attack on propene. Note that the addition reactions are at the high pressure limit. The subscripts refer to the specific reaction pathways.

For N_2 as the collision partner and assumming a step size down of 500 cm^{-1} we find at 0.1, 1.0 and 10 atm and at temperatures in excess of 700 K.

$$\log [k(N_2,0.1)/k_\infty] = -0.691+3.00\times10^{-3}T-3.55\times10^{-6}T^2+5.83\times10^{-10}T^3$$

$$\log [k(N_2,1.0)/k_\infty] = -1.119+3.73\times10^{-3}T-3.33\times10^{-6}T^2+4.68\times10^{-10}T^3$$

$$\log [k(N_2,10.0)/k_\infty] = -1.00+2.89\times10^{-3}T-2.08\times10^{-6}T^2+1.57\times10^{-10}T^3$$

Non-terminal addition leads to the formation of a hot radical, which can decompose. Note that at higher temperatures *n*-propyl radical is so unstable that it can also decompose rapidly through a purely thermal reaction. In the lower temperature region some stabilization can occur and the possibilities are summarized in Tables 3 and 4. The presence of a decomposition channel makes the high pressure addition rate the actual value over most applicable conditions. Under the same conditions as for the terminal addition, the branching ratio for decompostion versus addition are as follows

$$\log [k_{a'}/k_{a+a'}(N_2,\ 0.10] = -2.324 + 5.904\times10^{-3}T - 4.946\times10^{-6}T^2 + 1.363\times10^{-9}T^3$$

$$\log [k_{d'}/k_{d+d'}(N_2,\ 1.0\ ] = -4.737 + 1.075\times10^{-2}T - 8.180\times10^{-6}T^2 + 2.080\times10^{-9}T^3$$

$$\log [k_{d'}/k_{d+d'}(N_2,\ 10.0] = -5.946 + 1.045\times10^{-2}T - 6.033\times10^{-6}T^2 + 1.130\times10^{-9}T^3$$

TABLE 1. Log $k_e/k_{e\infty}$ for terminal addition of hydrogen to propene as a function of temperature and pressure assumming strong collisions

log [M]	T/K				
	500	700	900	1100	1300
16.0	−0.19	−0.44	−0.77	−1.14	−1.51
16.5	−0.10	−0.27	−0.53	−0.84	−1.16
17.0	−0.04	−0.15	−0.34	−0.58	−0.85
17.5	−0.02	−0.08	−0.20	−0.37	−0.58
18.0	−0.03	−0.10	−0.22	−0.37	
18.5	−0.01	−0.05	−0.11	−0.21	
19.0	−0.02	−0.05	−0.10		
19.5	−0.02	−0.05			
20.0	−0.02				
20.5					

TABLE 2. Collisional efficiency for isopropyl radical formation as a function of temperature and downward step size

T/K	Step-size (cm^{-1})				
	150	300	600	1200	2400
500	5.21×10^{-2}	1.38×10^{-1}	2.94×10^{-1}	4.94×10^{-1}	6.81×10^{-1}
700	2.39×10^{-2}	7.18×10^{-2}	1.79×10^{-1}	3.53×10^{-1}	5.56×10^{-1}
900	1.13×10^{-2}	3.70×10^{-2}	1.04×10^{-1}	2.38×10^{-1}	4.30×10^{-1}
1100	5.38×10^{-3}	1.87×10^{-2}	5.79×10^{-2}	1.51×10^{-1}	3.13×10^{-1}
1300	2.80×10^{-3}	1.01×10^{-2}	3.36×10^{-2}	9.67×10^{-2}	2.28×10^{-1}

TABLE 3. Branching ratio log $k_{d'}/k_d+k_{d'}$ as a function of temperature and pressure assuming strong collisions

log [M]	T/K				
	500	700	900	1100	1300
16.0	−0.04	−0.02	−0.01		
16.5	−0.11	−0.05	−0.02	−0.01	
17.0	−0.25	−0.13	−0.06	−0.03	−0.01
17.5	−0.48	−0.26	−0.14	−0.07	−0.04
18.0	−0.81	−0.48	−0.28	−0.16	−0.09
18.5	−1.22	−0.79	−0.49	−0.31	−0.19
19.0	−1.67	−1.17	−0.80	−0.54	−0.36
19.5	−2.15	−1.62	−1.18	−0.86	−0.62
20.0	−2.65	−2.10	−1.63	−1.26	−0.97
20.5	−3.15	−2.59	−2.10	−1.71	−1.39
21.0	−3.65	−3.08	−2.60	−2.19	−1.86

TABLE 4. Collision efficiency for the non-terminal addition of hydrogen atom to propene as a function of temperature and downward step size

T/K	Step-size (cm^{-1})				
	150	300	600	1200	2400
500	4.99×10^{-2}	1.33×10^{-1}	2.86×10^{-1}	4.86×10^{-1}	6.75×10^{-1}
700	2.23×10^{-2}	6.76×10^{-2}	1.70×10^{-1}	3.41×10^{-1}	5.44×10^{-1}
900	1.04×10^{-2}	3.44×10^{-2}	9.78×10^{-2}	2.27×10^{-1}	4.17×10^{-1}
1100	5.28×10^{-3}	1.84×10^{-2}	5.69×10^{-2}	1.48×10^{-1}	3.09×10^{-1}
1300	2.97×10^{-3}	1.07×10^{-2}	3.49×10^{-2}	9.88×10^{-2}	2.28×10^{-1}

Comments

We conclude that abstraction of allylic hydrogens and non-terminal addition leading to displacement can be expected to the most important processes under combustion conditions.

References

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Kerr, J. A. and Parsonage, M. J., Evaluated Kinetic Data on Gas Phase Addition Reactions", Butterworths, London, 1972..

Wing Tsang
January, 1990

46,5 $C_3H_6 + O \rightarrow OC_3H_6$ $\rightarrow CH_2CO + CH_3 + H$ (a)
$\rightarrow CH_3CHCO + 2H$ (b)
$\rightarrow C_2H_5 + HCO$ (c)
$\rightarrow C_3H_5(\text{allyl}) + OH$ (d)
$\rightarrow CH{=}CHCH_3 + OH$ (e)
$\rightarrow CH_2{=}CCH_3 + OH$ (f)

	Conditions		Reaction rate constant	Uncertainty
Reference	T range/K	[M] range/cm^3	k/cm^{3}molecule^{-1}s^{-1}	
Fontijn and Mahmud (1989)	300–1215	$2.5–11.1\times10^{18}$ CO_2 or O_2 $3.7–100\times10^{12}$ C_3H_6. Resonance Fluorescence detection of photolytically generated O-atoms	$k_{a+b+c+d+e+f}=$ $2.6\times10^{-16}T^{1.6}\exp(316/T)$	1.5
Cvetanovic (1987) (review)	290–450		$k_{a+b+c+d+e+f}=$ $1.01\times10^{-11}\exp(-280/T)$	1.1
Perry (1983)	258–861	$2–7.5\times10^{14}O_2$ $2–7.5\times10^{15}NO$ in $2–80\times10^{12}$ C_3H_6 in $4–32\times10^{17}$ Ar O-atom detection from chemiluminescence reaction $O+NO+M\rightarrow M+NO_2^*\rightarrow NO_2+h\nu$	$k_{a+b+c+d+e+f}=3.4\times10^{-19}T^{2.56}$ $\exp(569/T)$	1.2
Recommendations:			$k_{a+b+c+d+e+f}=6\times10^{-18}T^{2.15}\exp(400/T)$ $k_d=2.9\times10^{-13}T^{0.7}\exp(-2961/T)$ $k_e=2\times10^{-13}T^{0.7}\exp(-4509/T)$ $k_f=1\times10^{-13}T^{0.7}\exp(-3841/T)$ $k_{a+b+c}=5.8\times10^{-17}T^{1.83}\exp(275/T)$ $k_a/k_b=2$ $k_{a+b}/k_{a+b+c}=3.4\exp(-650/T)$	1.2 3 3 3 1.5 1.3 2

Comments

The interactions of ground state oxygen atoms and propylene are very complex. The experimental results given in terms of the total rate constant for the reaction of propylene with oxygen atoms are quite accurate. The general picture and our recommendations are summarized in Fig. 1. The recommendations on the total rate constants are based on an average of the three references quoted above. This leads to the rate expression

$$k_{a+b+c+d+e+f} = 6\times10^{-18}T^{2.15}\exp(400/T)\ \text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$$

with an uncertainty of a factor of 1.3 up to 1200 K, increasing to a factor of 3 at 2500 K.

The most serious uncertainties are in the branching ratios. There are no measurments on the contribution to the total rate constants from abstraction processes. Our estimates are based on the observation that OH and O abstraction reactions generally track each other. We have therefore determined the rate expression for the abstraction of allylic hydrogens from the relation

$$k(\mathrm{O+C_3H_6 \rightarrow C_3H_5+HO}) =$$
$$[k(\mathrm{O+C_2H_6 \rightarrow C_2H_5+HO})/k(\mathrm{OH+C_2H_6 \rightarrow C_2H_5+H_2O})]^*$$
$$k(\mathrm{OH+C_3H_6 \rightarrow C_3H_5+H_2O}).$$

This leads to the rate expression

$$k_d=2.9\times10^{-13}T^{0.7}\exp(-2961/T)\mathrm{cm^3molecule^{-1}s^{-1}}$$

In a similar fashion from the relative rate expressions for OH attack on allylic and vinylic hydrogens, we find

$$k_e=2\times10^{-13}T^{0.7}\exp(-4509/T)\mathrm{cm^3molecule^{-1}s^{-1}}$$
$$k_f=1\times10^{-13}T^{0.7}\exp(-3841/T)\mathrm{cm^3molecule^{-1}s^{-1}}$$

Comparison with the the recommended total rate expression suggest that abstraction channels will probably not be the main reaction process at any reasonable temperature. Subtracting these expressions from the recommended expression for the total process leads to the following expression for the purely addition process.

$$k_{a+b+c}=5.8\times10^{-17}T^{1.83}\exp(275/T)\mathrm{cm^3molecule^{-1}s^{-1}}$$

There are two channels for the addition reaction. They involve a pressure independent displacement process and addition to form a biradical and its subsequent decomposition. The general situation has been reviewed by Cvetanovic and Singleton and our recommendations are based on their analysis. Near room temperature about 30% of the oxygen reacts via the pressure independent process. The displacment of the methyl group is favored by a ratio of 2 to 1. Thus

$$k_a/k_b=2$$

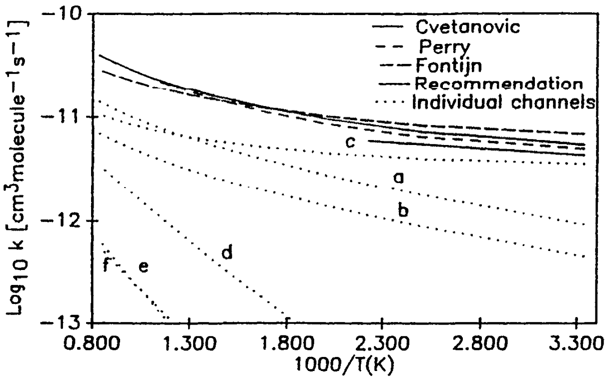

FIG. 1. Experimental results and recommendation for rate constants for O attack on propene.The subscripts refer to the specific reaction channels. Experimental measurements are all for total rate constants.

The only existing data on temperature dependence of the two processes deal with 1-butene. From 298 K to 473K the relative ratios of the contributions from the pressure independent and pressure dependent process (at the high pressure limit) increase from 0.3 to 0.6. This indicates an activation energy near 6 kJ/mol. We therefore use this to scale our data to higher temperatures. The rate expression relating the two processes is

$$k_{a+b}/k_c=3.4\exp(-650/T)$$

With these relations rate expressions for all the individual steps can be derived. As written above we have assummed that they will decompose by ejection of the beta hydrogen leading to the formation of ketene and methyl ketene. We cannot rule out the possibility of a 1,2 hydrogen shift leading to the formation of acetyl and methylacetyl radicals. These will of course decompose rapidly to form methyl radical and CO and ethyl and CO. The recommendation given here assumes that this is a slow process compare to beta hydrogen ejection to form the ketenes.

The pressure dependent process involves the initial formation of propylene oxide and propionaldehyde. The initial products are chemically hot. Stabilization as well as fragmentation can occur. The latter will be favored under most combustion conditions. Accordingly we have expressed this reactions in terms of fragmentation to ethyl and formyl radical. At higher pressures and lower temperatures considerable stabilization can occur. However, it should be noted that in combustion systems O atoms are only found under very high temperature conditions and are in fact much less important than OH radicals in effecting the destruction of organic molecules.

References

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Mahmud, K. and Fontijn, A., "An HTP Kinetic Study of the reactionof O(^{3}P) Atoms with Propylene over the 300 to 1215 K Temperature Range, 22nd Symposium (International) on Combustion, The Combustion Institute, Pittsburgh Pa., (in press).

Perry, R. A., "Absolute Rate Constants for the Reaction of O(^{3}P) Atoms with Ethylene, Propylene and Propylene-d_6 over the Temperature Range 258–861 K", J. Chem. Phys., **80**, 153, (1984).

Wing Tsang
January, 1989

46,6 $C_3H_6 + OH \rightarrow HOC_3H_6$ (a)
$\rightarrow C_3H_5$(allyl) + H_2O (b)
$\rightarrow C_3H_5$(propenyl) + H_2O (c)
$\rightarrow C_3H_5$(propenyl-2) + H_2O (d)

	Conditions		Reaction rate constant	Uncertainty
Reference	T range/K	[M] range/cm^3	$k/cm^3 molecule^{-1}s^{-1}$	
Atkinson (1986) review			$k_a = 4.85 \times 10^{-12} exp(504/T)$	1.15
Tully and Goldsmith(1985)	700–896	Trace C_3H_6 in 5×10^{18} He OH from 190 nm photolysis of N_2O in H_2O	$k_b + k_c + k_d = 3.31 \times 10^{-11} exp(-1542/T)$	1.03
Baldwin *et al.*(1984)	723	0–3.7 × 10^{17} N_2 12–3.7 × 10^{17} O_2 with smaller amounts of tetremethylbutane and propene	$k_b < 1.2 \times 10^{-11}$ $k_c + k_d = 1.5 \times 10^{-10} exp(-3252/T)$	3
Smith *et al.*(1984)	960	1.5×10^{18} N_2	$k_b + k_c + k_d = 4.5$	2
	1090	3–12 × 10^{17} SF_6	5.8×10^{-12}	
	1180	3×10^{12} H_2O_2	7.0×10^{-12}	
	1210	Laser pyrolysis	9.0×10^{-12}	
Recommendations	300–600		$k_a = 4.85 \times 10^{-12} exp(504/T)$	1.15
	700–2500		$k_b = 5.18 \times 10^{-18} T^2 exp(150/T)$	1.2
			$k_c = 3.55 \times 10^{-18} T^2 exp(-1398/T)$	2
			$k_d = 1.8410^{-18} T^2 exp(-730/T)$	2

Comments

The rate expression for addition as recommended by Atkinson covers an enormous volume of work and is highly reliable.

At temperatures above 550 K the reaction is reversed. Thus for most combustion purposes the important process is abstraction. For this process, we favor the results of Tully and Goldsmith. This is within a factor of 3 of Baldwin et al's upper limit. The physical conditions under laser pyrolysis is somewhat uncertain and since this is a new method we regard it as essentially confirmatory of the work of Tully and Goldsmith. The rate expression given by these authors contains components from all three processes. Unfortunately there are no data on the branching ratios. Our recommendations are based on the results of Tully (Chemical Physics Letters, 1988, 143, 510) for the reaction of OH + ethylene and the rate constant ratio of OH+primary hydrogens in ethane by Tully *et al.*(J. Phys. Chem., 1986, 90, 691) to OH + secondary hydrogens from Droege and Tully (J. Phys. Chem., 1986, 90, 1949). For all three abstraction routes we have arbitrarily introduced a T^2 dependence in the A-factor. This resulted in the following rate expressions;

$$k_b = 5.18 \times 10^{-18} T^2 exp(150/T)\ cm^3 molecule^{-1}s^{-1}$$
$$k_c = 3.55 \times 10^{-18} T^2 exp(-1398/T)\ cm^3 molecule^{-1}s^{-1}$$
$$kd = 1.8410^{-18} T^2 exp(-730/T)\ cm^3 molecule^{-1}s^{-1}$$

A plot of our recommendations and the experimental results can be found in Fig. 1. The experimental results are estimated to be a factor of 1.2 for abstraction of an allylic hydrogen and factors of 2 for abstraction from vinylic moieties.

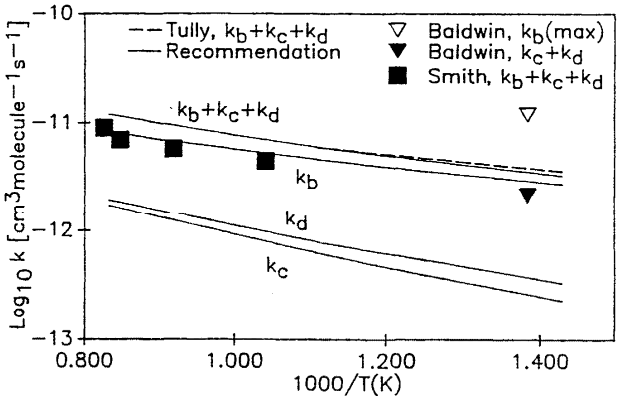

FIG. 1. Summary of recommendations and experimental measurements on the abstraction of hydrogen atoms by hydrogen from propene. Letters refer to specific reaction pathways.

The present analysis of the addition reaction may have simplified a much more complex situation. At the lower temperatures, where addition is the predominant process Tully and Goldsmith find evidence for hydrogen migration processes. This supports the observations of Hoyermann and Sieverts (Ber. Bunsenges. Phys. Chem., **83**, 933, 1979) from low pressure experiments where they find extensive cracking following the formation of the adduct. These effects may well be accentuated at higher temperatures. There is insufficient data to analyze the contributions from these effects.

Reference

Atkinson, R. "Kinetics and Mechanisms of the Gas Phase Reactions of the Hydroxyl Radical with Organic Compounds Under Atmospheric Conditions", Chem. Rev., **86**, 69, (1986).

Baldwin, R. R., Hisham, M. W. V., and Walker, R. W., "Elementary Reactions Involved in the Oxidation of Propene: Arrhenius Parameters for the Reaction HO_2 + C_3H_6 = C_3H_6O + OH" 20th Symposium on Combustion I (International), The Combustion Institute, 1984, 743.

Smith, G. P., Fairchild, P. W., Jeffries, J. B., Crosley, D. R., J. Phys. Chem., **89**, 1269, (1985).

Tully, F. P., and Goldsmith, J. E. M. Kinetics Study of the Hydroxyl Radical- Propene Reaction" Chemical Physics Letters, **116**, 345, (1985).

Wing Tsang
January, 1989

46,7 $C_3H_6 + HO_2 \rightarrow C_3H_6O + OH$ (a)
$\rightarrow$ allyl(C_3H_5) + H_2O_2 (b)

	Conditions		Reaction rate constant	Uncertainty
Reference	T range/K	[M] range/cm^3	$k/cm^3molecule^{-1}s^{-1}$	
Baldwin *et al.*(1984)	673–773	0–3.7×10^{17} N_2 12–3.7×10^{17} O_2 with smaller amounts of tetremethylbutane and propene	$k_a = 1.74\times10^{-12}\exp(-7149/T)$ $k_b < 0.2\,k_a$	3
Recommendation			$k_a = 1.74 \times 10\ ^{12}\exp(-7149/T)$ $k_b = 1.6\times10^{-20}T^{2.6}\exp(-7000/T)$	3 10

Comments

The work of Baldwin *et al.* is the only rate measurement on this reaction. It is based on a well established methodology and is referenced against the $HO_2 + HO_2$ reaction. For the abstraction reaction our recommendation is a rough estimate and is based on the observation that the existing data for radical attack on allylic hydrogen is close to that for the abstraction of a secondary hydrogen in alkanes. It leads to rate constants that are in accord with the limits set by Baldwin *et al.* We estimate the uncertainties at factors of 3 for k_a and an order of magnitude for k_b.

References

[1] Baldwin, R. R., Hisham, M. W. V., and Walker, R. W., "Elementary Reactions Involved in the Oxidation of Propene: Arrhenius Parameters for the Reaction HO_2 + C_3H_6 = C_3H_6O + OH" 20th Symposium on Combustion I (International), The Combustion Institute, 1984, p743.

W. Tsang
November, 1988

46,15 $C_3H_6 + HCO \rightarrow C_3H_5$ (allyl) + H_2CO

	Conditions		Reaction rate constant	Uncertainty
Reaction/Reference	T range/K	[M] range/cm^3	$k/cm^3molecule^{-1}s^{-1}$	
Recommendations			$1.8\times10^{-17}T^{1.9}\exp(-8558/T)$	10

Comments

There are no data. HCO can be expected to add to propene. However under combustion conditions the reaction can be expected to be reversed. The only other process is abstraction of an allylic hydrogen. We assume as in other cases of the abstraction of an allylic hydrogen that the rate constant will be similar to that for the abstraction of a secondary hydrogen. This leads to the rate expression;

$$k(C_3H_6 + HCO \rightarrow C_3H_5 + H_2CO) = 1.8\times10^{-17}T^{1.9}\exp(-8558/T)cm^3molecule^{-1}s^{-1}$$

The uncertainty is a factor of 10.

W. Tsang
September, 1988

46,16 $C_3H_6 + CH_3 \rightarrow s\text{-}C_4H_9$ **(a)**
$\rightarrow i\text{-}C_4H_9$ **(b)**
$\rightarrow$ **(allyl)** $C_3H_5 + CH_4$ **(c)**
$\rightarrow$ **(1-propenyl)** $C_3H_5 + CH_4$ **(d)**
$\rightarrow$ **(2-propenyl)** $C_3H_5 + CH_4$ **(e)**

	Conditions		Reaction rate constant	Uncertainty
Reaction/Reference	T Range/k	[M] Range/cm^3	k/cm^{3}molecule^{-1}s^{-1}	
Kerr and Parsonage (1976) review	350–600		$k_c+k_d+k_e=2.3\times10^{-13}\exp(-4330/T)$	1.4
Kerr and Parsonage (1972) review	350–450		$k_a = 2.8\times10^{-13}\exp(-3726/T)$ $k_b = 0.1\text{x}k_a$	1.4
Recommendations			$k_a= 2.8\times10^{-13}\exp(-3726/T)$ $k_b= 1.6\times10^{-13}\exp(-4028/T)$ $\text{Log}\,(k_b/k_{b\infty}) = -1.2271$ $+5.0893\times10^{-3}T-6.5040\times10^{-6}T^2$ $+2.6606\times10^{-9}T^3-3.7825\times10^{-13}T^4$ $k_c=3.68\times10^{-24}T^{3.5}\exp(-2856/T)$ $k_d/k_c=0.61\exp(-3610/T)$ $k_e/k_c=0.38\exp(-3010/T)$	1.4 3.0 1.4 6 6

Comments

The rate expression for abstraction as recommended by Kerr and Parsonage (1976) is probably due to abstraction of the allylic hydrogen. At higher temperatures we expect that abstraction of the vinylic hydrogens can occur. However the recommendations of Kerr and Parsonage ("Evaluated Kinetic Data on Gas Phase Hydrogen Transfer Reactions of Methyl Radicals" Butterworths, London and Boston, 1976) for abstraction of a vinylic hydrogen from ethylene leads to rate constants that are unreasonably large. For example the ratio of rate constants for OH attacking propene and ethylene is actually larger than that for methyl attack. Thermochemistry dictates that methyl attack will be more selective. It is possible that the experimental observations have important contributions from the sequence of reactions, $CH_3+C_2H_4 \rightarrow n\text{-}C_3H_7$; $n\text{-}C_3H_7+CH_3 \rightarrow CH_4+C_3H_6$. The observed methane is thus not an abstraction product. We tentatively suggest the use of the values derived from the relation $0.5\times k(H+C_2H_4 \rightarrow C_2H_3 + H_2)*k(CH_3+C_3H_8 \rightarrow CH_4+ n\text{-}C_3H_7)/k(H+C_3H_8 \rightarrow n\text{-}C_3H_7+H_2)$ for the abstraction of the primary vinylic hydrogens. For the secondary vinylic hydrogen we assume that the effect is the same as in methyl attack on alkanes. This leads to the following rate expressions;

$$k_c=3.68\times10^{-24}T^{3.5}\exp(-2856/T)$$

$$k_d/k_c=0.61\exp(-3610/T)$$

$$k_e/k_c=0.38\exp(-3010/T)$$

with an uncertainty of a factor of 1.4 for k_c and factors of 6 for k_d and k_e.

We accept the recommendations of Kerr and Parsonage (1972) for terminal addition. Under most combustion conditions this process will be reversed at the higher temperatures commensurate with combustion conditions. For non terminal addition our recommendation is consistent (through the thermochemistry) with the rate expression for the decomposition of isobutyl radical (45,1). In the case of the terminal addition, the main reaction, our recommendation is based on the following rate expression for decomposition $k(s\text{-}C_4H_9 \rightarrow C_3H_6 + CH_3) = 9.3\times10^{12}\exp(-14766/T)\ s^{-1}$. This demonstrates that under most combustion conditions the reaction will also be reversed. Fall-off behavior for non-terminal addition is summarized inTables 1 and 2 These tables are for the formation of isobutyl radicals. They should also be applicable for s-butyl radical formation.

A plot of our recommendations can be found in Fig. 1.

TABLE 1. Log k/k_∞ as a function of temperature and pressure assumming strong collisions for the formation of s-butyl and isobutyl radicals

log [M]	T/K										
	500	700	900	1100	1300	1500	1700	1900	2100	2300	2500
16.0	−0.14	−0.43	−0.83	−1.28	−1.74	−2.16	−2.54	−2.88	−3.16	−3.41	−3.61
16.5	−0.07	−0.26	−0.57	−0.95	−1.34	−1.73	−2.08	−2.40	−2.67	−2.91	−3.12
17.0	−0.03	−0.14	−0.36	−0.66	−0.98	−1.32	−1.64	−1.93	−2.19	−2.42	−2.62
17.5	−0.01	−0.07	−0.21	−0.42	−0.67	−0.95	−1.22	−1.49	−1.73	−1.94	−2.13
18.0		−0.03	−0.11	−0.24	−0.42	−0.63	−0.86	−1.08	−1.29	−1.48	−1.66
18.5		−0.01	−0.05	−0.12	−0.23	−0.38	−0.55	−0.72	−0.89	−1.06	−1.21
19.0			−0.02	−0.05	−0.11	−0.20	−0.31	−0.43	−0.56	−0.69	−0.81
19.5			−0.01	−0.02	−0.05	−0.09	−0.15	−0.22	−0.31	−0.40	−0.49
20.0					−0.02	−0.04	−0.06	−0.10	−0.14	−0.19	−0.25
20.5					−0.01	−0.01	−0.01	−0.01	−0.02	−0.03	−0.04
21.0							−0.01	−0.01	−0.02	−0.03	−0.04

TABLE 2. Collision efficiency for s-butyl and isobutyl radical formation as a function of temperature and downward step size

T/K	Step-size (cm^{-1})				
	150	300	600	1200	2400
500	3.91×10^{-2}	1.09×10^{-1}	2.46×10^{-1}	4.40×10^{-1}	6.36×10^{-1}
700	1.41×10^{-2}	4.52×10^{-2}	1.23×10^{-1}	2.70×10^{-1}	4.69×10^{-1}
900	6.27×10^{-3}	2.17×10^{-2}	6.68×10^{-2}	1.72×10^{-1}	3.55×10^{-1}
1100	4.25×10^{-3}	1.53×10^{-2}	5.05×10^{-2}	1.44×10^{-1}	3.40×10^{-1}
1300	4.12×10^{-3}	1.51×10^{-2}	5.17×10^{-2}	1.57×10^{-1}	4.06×10^{-1}
1500	4.82×10^{-3}	1.78×10^{-2}	6.16×10^{-2}	1.92×10^{-1}	5.23×10^{-1}
1700	5.96×10^{-3}	2.20×10^{-2}	7.59×10^{-2}	2.37×10^{-1}	6.58×10^{-1}
1900	7.29×10^{-3}	2.67×10^{-2}	9.17×10^{-2}	2.85×10^{-1}	7.87×10^{-1}
2100	8.62×10^{-3}	3.15×10^{-2}	1.07×10^{-1}	3.30×10^{-1}	9.03×10^{-1}
2300	9.87×10^{-3}	3.59×10^{-2}	1.21×10^{-1}	3.70×10^{-1}	1.00
2500	1.10×10^{-2}	3.99×10^{-2}	1.33×10^{-1}	4.06×10^{-1}	1.09

Comments

We recommend the following expressions for fall off behavior at 0.1, 1.0 and 10 atm. over the temperature range 900–2500K with N_2 and butyl radical itself at the third body. They are based on the assumption that the step size down for N_2 and butyl radical is 500 cm^{-1} and 1000 cm^{-1} respectively.

$$\log(k/k_\infty, N_2, 0.1) = -1.1968 + 5.9983\times10^{-3}T - 9.0618\times10^{-6}T^2 + 4.0598\times10^{-9}T^3 - 6.1315\times10^{-13}T^4$$

$$\log(k/k_\infty, N_2, 1.0) = -1.2271 + 5.0893\times10^{-3}T - 6.5040\times10^{-6}T^2 + 2.6606\times10^{-9}T^3 - 3.7825\times10^{-13}T^4$$

$$\log(k/k_\infty, N_2, 10.0) = -0.3170 + 1.2050\times10^{-3}T - 1.2363\times10^{-6}T^2 + 2.3271\times10^{-10}T^3$$

$$\log(k/k_\infty, C_4H_8, 0.1) = -1.1581 + 5.2093\times10^{-3}T - 7.1843\times10^{-6}T^2 + 3.0468\times10^{-9}T^3 - 4.4377\times10^{-13}T^4$$

$$\log(k/k_\infty, C_4H_8, 1.0) = -0.2772 + 1.2508\times10^{-3}T - 1.4707\times10^{-6}T^2 + 2.9286\times10^{-10}T^3$$

$$\log(k/k_\infty, C_4H_8, 10.0) = -0.2226 + 7.4630\times10^{-4}T - 6.6952\times10^{-7}T^2 + 1.0416\times10^{-10}T^3$$

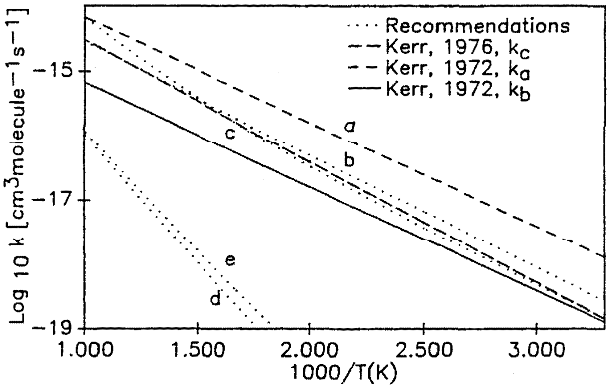

FIG. 1. Rate constants as a function of temperature for methyl attack on propene. Recommendation for k_a coincides with Kerr (1972).

References

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

Kerr, J. A. and Parsonage, M. J. "Evaluated Kinetic Data on Gas Phase Addition Reactions of Atoms and Radicals with Alkenes, Alkynes and Aromatic Compounds" Butteworths, London and Boston, 1972.

Wing Tsang
August, 1988

46,17 $C_3H_6 + C_2H_5 \rightarrow$ (allyl) $C_3H_5 + C_2H_6$ (a)
$\rightarrow C_2H_4 + n\text{-}C_3H_7$ (b)

	Conditions		Reaction rate constant	Uncertainty
Reference	T range/K	[M] range/cm^3	k/cm^{3}molecule^{-1}s^{-1}	
Recommendations			$k_a = 3.7\times10^{-24}T^{3.5}\exp(-3340/T)$ $k_{total} = 1.7\times10^{-13}\exp(-3625/T)$ $k_b/k_{total} = 1/(1+0.66\exp(1000/T)$	3 2 3

Comments

There are no measurements on the rate constants for these processes. Our estimates are based on the recommendations for $C_3H_6 + CH_3$ (46,16) and an increased activation energy of 4kJ/mol. This leads to the expression

$$k_a = 3.7\times10^{-24}T^{3.5}\exp(-3340/T)\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$$

with an uncertainty of a factor of 3.

For the addition reaction, making use of the general trends noted by Kerr and Parsonage, ("Evaluated Kinetic Data on Gas Phase Addition Reactions: Reactions of Atoms and Radical with Alkenes, Alkynes and Aromatic Compounds" Butterworths, London, 1972), we suggest the rate of terminal addition will be

$$k_{total} = 1.7\times10^{-13}\exp(-3625/T)\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$$

with an uncertainty of a factor of 2. Under most combustion conditions alkyl radicals will decompose, therefore the reaction will be reversed. However the 2-pentyl radical can isomerize to the 1-pentyl species through 1,4 hydrogen migration. If this is fast, a rough estimate of the contribution from channel b will be

$$k_b/k_{total} = 1/(1+0.67\exp(1000/T))$$

with an estimated uncertainty of a factor of 3. The nonterminal addition to propene is expected to be slower. Furthermore, the newly formed radical has no chance of undergoing hydrogen migration. Thus its most likely fate is decomposition to the starting products.

W. Tsang
September, 1988

46,18 $C_3H_6 + C_2H_4 \rightarrow$ **1-pentene (a)**
$\rightarrow C_3H_5(\text{allyl}) + C_2H_5$ **(b)**
$\rightarrow n\text{-}C_3H_7 + C_2H_3$ **(c)**
$\rightarrow \text{i-}C_3H_7 + C_2H_3$ **(d)**

	Conditions		Reaction rate constant	Uncertainty
Reference	T range/K	[M] range/cm^3	k/cm^{3}molecule^{-1}s^{-1}	
Log K_p(a) $= -6.467 + 3.925 \times 10^3/T + 3.308 \times 10^5/T^2 - 3.581 \times 107/T^3$				
Log K_p(b) $= 1.380 - 1.135 \times 10^4/T + 1.947 \times 10^3/T^2 + 4.368 \times 10^6/T^3$				
Log K_p(c) $= 1.759 - 1.652 \times 10^4/T + 5.586 \times 10_3/T_2 + 2.131 \times 10^6/T^3$				
Log K_p(d) $= 1.367 - 1.576 \times 10^4/T - 1.098 \times 10^5/T^2 + 1.418 \times 10^7/T^3$				
Recommendations:			$k_a = 5.3 \times 10^{-21} T^{2.2} \exp(-17151/T)$	1.5
			$k_b = 9.6 \times 10^{-11} \exp(-25958/T)$	3
			$k_c = 1 \times 10^{-10} \exp(-37966/T)$	3
			$k_d = 1.2 \times 10^{-8} T^{-0.65} \exp(-37051/T)$	3

Comments

There are no data on the kinetics of these reactions. We have calculated k_a from the rate expression of the reverse process (W. Tsang, Int. J. Chem. Kin., **10**, 599 (1978)) and the thermodynamic properties of the molecules. Similarly, k_b, k_c and k_d have been derived from the recommended rate expressions for the reverse processes ((47,17), (41,19) and (42,19))and the equilibrium constants. On this basis we obtain the following rate expressions.

$k_a = 5.3 \times 10^{-21} T^{2.2} \exp(-17151/T)$ cm^{3}molecule^{-1}s^{-1}
$k_b = 9.6 \times 10^{-11} \exp(-25958/T)$ cm^{3}molecule^{-1}s^{-1}
$k_c = 1 \times 10^{-10} \exp(-37966/T)$ cm^{3}molecule^{-1}s^{-1}
$k_d = 1.2 \times 10^{-8} T^{-0.65} \exp(-37051/T)$ cm^{3}molecule^{-1}s^{-1}

The estimated uncertainties are factors of 1.5, 3, 3 and 3 respectively.

W. Tsang
September, 1988

46,19 $C_3H_6 + C_2H_3 \rightarrow C_3H_5(\text{allyl}) + C_2H_4$ **(a)**
$\rightarrow C_3H_5(\text{1-propenyl}) + C_2H_4$ **(b)**
$\rightarrow C_3H_5(\text{2-propenyl-2}) + C_2H_4$**(c)**
$\rightarrow 1{,}3\text{-}C_4H_6 + CH_3$**(d)**
$\rightarrow 1{,}3\text{-}C_5H_{10} + H$**(e)**

	Conditions		Reaction rate constant	Uncertainty
Reactions/Reference	T range/K	[M] range/cm^3	k/cm^{3}molecule^{-1}s^{-1}	
Recommendations			$k_a = 3.68 \times 10^{-24} T^{3.5} \exp(-2356/T)$	6
			$k_b/k_a = 0.61 \exp(-3110/T)$	6
			$k_c/k_a = 0.38 \exp(-2510/T)$	6
			$k_d = 1.2 \times 10^{-12} \exp(-2520/T)$	3
			$k_e = 1.2 \times 10^{-12} \exp(-3240/T)$	3

Comments

There are no data on the rate constants for these reactions. For the abstraction processes we have taken the comparable rate expressions for CH_3 attack on propene and decreased the activation energy by 4 kJ/mol. This leads to

$k_a = 3.68 \times 10^{-24} T^{3.5} \exp(-2356/T)$ cm^{3}molecule^{-1}s^{-1}
$k_b/k_a = 0.61 \exp(-3110/T)$ cm^{3}molecule^{-1}s^{-1}
$k_c/k_a = 0.38 \exp(-2510/T)$ cm^{3}molecule^{-1}s^{-1}

with an estimated uncertainty of a factor of 6.

For the displacement reactions, our estimates are based on the measurements of Fahr and Stein (22nd Symposium on Combustion (International), The Combustion Institute, Pittsburgh, Pa, 1988, 1023). They determined at 1100 K the rate constant for vinyl addition to ethylene and acetylene and found them to be 2.4×10^{-13} and 3.3×10^{-13} cm^{3}molecule^{-1}s^{-1} respectively. In combination with room temperature results they estimate the rate expression for vinyl displacement of hydrogen from acetylene to be $3.3 \times 10^{-12} \exp(-2520/T)$

$cm^3 molecule^{-1} s^{-1}$. On this basis we estimate the comparable rate expression for vinyl displacement of the vinylic hydrogen from ethylene to be;

$$k_d = 1.2\times10^{-12}\exp(-2520/T)\ cm^3 molecule^{-1} s^{-1}$$

with an uncertainty of a factor of 3. For displacement of the methyl group as a result of non-terminal addition, we recommend an activation energy that is 6 kJ higher, in conformity with the situation for hydrogen displacement of methyl from propene. This leads to the expression;

$$k_e = 1.2\times10^{-12}\exp(-3240/T)\ cm^3 molecule^{-1} s^{-1}$$

The uncertainties for these two processes are a factor of 3 near 1100 K.

W. Tsang
June, 1988

46,20 $C_3H_6 + C_2H_2 \rightarrow C_3H_5 + C_2H_3$

	Conditions		Reaction rate constant	Uncertainty
Reaction/Reference	T range/K	[M] range/cm^3	$k/cm^3 molecule^{-1} s^{-1}$	
$\log K_p = 0.8955 - 1.004\times10^4/T - 1.333\times10^4/T^2 + 1.812\times10^7/T_3$				
Recommendations			$6.7\times10^{-11}\exp(-23560/T)$	2.5

Comments

There are no data for the kinetics of this process. We have used our recommendation for the rate expression of the reverse reaction (47,19) and the thermodynamics to derive the recommended rate expression

$$6.7\times10^{-11}\exp(-23560/T)\ cm^3 molecule^{-1} s^{-1}$$

given here. The estimated uncertainty is a factor of 2.5. Note that the alternative processes to form 1,4 pentadiene and propyl plus C_2H have rate constants that are signficantly smaller than that recommended here.

W. Tsang
August, 1988

46,21 $C_3H_6 + C_2H \rightarrow$ 1-butyne + H (a)
$\rightarrow$ 1-propyne + CH_3 (b)
$\rightarrow C_3H_5$ (allyl) + C_2H_2 (c)
$\rightarrow$ 1-propenyl + C_2H_2 (d)
$\rightarrow$ 2-propenyl + C_2H_2 (e)

	Conditions		Reaction rate constant	Uncertainty
Reaction/Reference	T range/K	[M] range/cm^3	$k/cm^3 molecule^{-1} s^{-1}$	
Recommendations			$k_a = 2\times10^{-11}$	2.5
			$k_b = 2\times10^{-11}$	2.5
			$k_c = 6\times10^{-12}$	3
			$k_d = 2\times10^{-12}$	5
			$k_e = 2\times10^{-12}$	5

Comments

There are no data on the rates of these processes. C_2H is an extremely reactive radical. Using the measured rate constant for $C_2H + C_2H_2$ (21,20) as a base we estimate that k_a and k_b will be one-half this value,or

$$k_a = k_b = 2\times10^{-11}\ cm^3 molecule^{-1} s^{-1}$$

with an uncertainty of a factor of 2.5.

For the abstraction process, we recommend for the allylic hydrogen the rate expression for $C_2H + C_2H_6$ (21,11) or

$$k_c = 6\times10^{-12}\ cm^3 molecule^{-1} s^{-1}$$

with an uncertainty of a factor of 3. Finally for abstraction of the vinylic hydrogens we believe that the rate constants should be somewhat smaller than that for k_c or

$$k_d = k_e = 2\times10^{-12}\ cm^3 molecule^{-1} s^{-1}$$

with an uncertainty of a factor of 5.

W. Tsang
August, 1988

46,22 $C_3H_6+CH_3OO \rightarrow C_3H_6O + CH_3O$ (a)
$\rightarrow C_3H_5 + CH_3OOH$ (b)

	Conditions		Reaction rate constant	Uncertainty
Reaction/Reference	T range/K	[M] range/cm^3	k/cm^{3}molecule^{-1}s^{-1}	
Recommendations			$k_a=6.6\times10^{-13}\exp(-5900/T)$ $k_b=3.3\times10^{-12}\exp(-8581/T)$	4 10

Comments

There are no measurements on the rate constants for these processes. Osborne and Waddington (J. Chem. Soc., Perkin 2, 1980, 925) have determined the rate constant for methylperoxy addition to a series of olefins and established a correlation between the rate constant at any temperature and the ionization energy. On this basis, we estimate

$$k_a = 6.6\times10^{-13}\exp(-5900/T)\ \mathrm{cm^3molecule^{-1}s^{-1}}$$

with an uncertainty of a factor of 4.

For the abstraction reaction, as in all other cases we assume that the rate expression for abstraction of an allylic hydrogen will be close to that for the abstraction of a secondary hydrogen atom. This leads to;

$$k_b = 3.3\times10^{-12}\exp(-8581/T)\ \mathrm{cm^3molecule^{-1}s^{-1}}$$

with an uncertainty of a factor of 10.

W. Tsang
October, 1988

46,23 $C_3H_6 + CH_3CO \rightarrow C_3H_5 + CH_3CHO$

	Conditions		Reaction rate constant	Uncertainty
Reaction/Reference	T range/K	[M] range/cm^3	k/cm^{3}molecule^{-1}s^{-1}	
Recommendations			$8.8\times10^{-18}T^2\exp(-8173/T)$	10

Comments

There are no data on the kinetics of this process. In line with other reactions we have assummed that the rate constant for the abstraction of an allylic hydrogen is close to that of a secondary hydrogen. This leads to

$$k(C_3H_6+CH_3CO \rightarrow C_3H_5+CH_3CHO) = 8.8\times10^{-18}T^2\exp(-8173/T)\mathrm{cm^3molecule^{-1}s^{-1}}$$

The uncertainty is a factor of 10. The addition process will be readily reversed under combustion conditions.

Wing Tsang
June, 1988

46,24 $C_3H_6 + CH_3O \rightarrow C_3H_5 + CH_3OH$

	Conditions		Reaction rate constant	Uncertainty
Reaction/Reference	T range/K	[M] range/cm^3	k/cm^{3}molecule^{-1}s^{-1}	
Recommendations			$90T^{2.95}\exp(-6032/T)$	10

Comments

There are no data on the rate constants for this reaction. Addition will be readily reversed under combustion conditions. We assume that 1,4 hydrogen migration is not competitive with decomposition. The most likely reaction possibility is abstraction of the allylic hydrogen for which we assign a rate expression equal to our recommendation for methoxy attack on the secondary hydrogens in propane.

$$k(C_3H_6+CH_3O\rightarrow C_3H_5+CH_3OH) = 90T^{2.95}\exp(-6032/T)\ \mathrm{cm^3molecule^{-1}s^{-1}}.$$

The uncertainty is a factor of 10.

Wing Tsang
June, 1988

46,25 $C_3H_6 + {}^1CH_2 \rightarrow {}^3CH_2 + C_3H_6$ (a)
$\rightarrow C_3H_5 + CH_3$ (b)
$\rightarrow 2\text{-}C_4H_8$ (c)
$\rightarrow i\text{-}C_4H_8$ (d)

	Conditions		Reaction rate constant	Uncertainty
Reaction/Reference	T range/K	[M] range/cm³	k/cm³molecule⁻¹s⁻¹	
Krzyanowski and Cvetanovic (1966)(also review)	296.5 K	$1-2\times10^{19}$ olefins 9% ketene photolysis of ketene at 260 nm	$k_{total}/k({}^1CH_2+C_2H_4)=1.3$ $k_{2+3+4+5+6}/k_{total}=0.66$ $k_{3'+4'}/k_{total}=0.19$ $k_{5'+6'+7'+8'}=0.15$	1.3
Recommendations			$k_a=5\times10^{-11}$ $k_b=8.7\times10^{-11}$ $k_c=7.2\times10^{-11}$ $k_d=0.9\times10^{-11}$	1.5 5 5 5

Comments

Singlet methylene will insert into the double bond and C−H bonds in propylene. There are a large number of possible reaction pathways. Some of the more important are given below;

${}^1CH_2 + C_3H_6 \rightarrow {}^3CH_2 + C_3H_6$ (1)
$\rightarrow c\text{-}C_3H_5CH_3$ (2)
$\rightarrow 1\text{-}C_4H_8$ (3)(3′)
$\rightarrow CC_3H_5 + CH_3$ (4)(4′)
$\rightarrow 2\text{-}C_4H_8$ (5)(5′)
$\rightarrow C_4H_7 + H$ (6)(6′)
$\rightarrow i\text{-}C_4H_8$ (7′)
$\rightarrow i\text{-}C_4H_7 + H$ (8′)

where the prime and unprimed quantities refer to products formed as a result of insertion into the C−H and C=C bonds respectively. We have tried to simplify the mechanism by grouping the expected products together in terms of processes a to d. Although there are no direct measurements, the results of Kryzanowski and Cvetanovic lead to a set of rate constants at limiting high pressures. Due to the fact that the rate constants are practically collisonal we assume that they will have no temperature dependence. From the data on single methylene attack on C_2H_4 (25,20) or $k({}^1CH_2 + C_2H_4)$ = 1.3×10^{-10} cm³molecule⁻¹s⁻¹ (where we have reduced the measured rate constant of Langford *et al*. (J. Chem. Phys. **78**, 6650, 1983) to take into account the rate constant for conversion of the singlet to the triplet as determined by Bohland *et al*. (Ber. Bunsenges. Phys. Chem., **89**, 1013, 1985) we obtain;

$k_{total} = 1.7\times10^{-10}$ cm³molecule⁻¹s⁻¹

This yields;

$k_{2+3+4+5} = 1.1\times10^{-10}$cm³molecule⁻¹s⁻¹
$k_{3'+4'} = 3.2\times10^{-11}$cm³molecule⁻¹s⁻¹
$k_{5'+6'} = 1.8\times10^{-11}$cm³molecule⁻¹s⁻¹
$k_{7'+8'} = 0.9\times10^{-11}$cm³molecule⁻¹s⁻¹

with an estimated error of 1.5 near room temperature and increasing to a factor of 5 at the highest temperatures. We have assummed that insertion to the vinylic bonds is uneffected by methyl substitution. For the conversion of ${}^1CH_2$ to ${}^3CH_2$ we assume the ratio for intersystem crossing versus reaction for propane as determined by Bohland *et al*.(Ber. Bunsenges. Phys. Chem., **89**, 1013, 1985) and arrive at

$k_1 = 5\times10^{-11}$ cm³molecule⁻¹s⁻¹

with an uncertainty of a factor of 1.5 near room temperature. The hot molecules that are formed via insertion can be stabilized or decompose. In the case of methylcyclopropane the principal mode of decomposition is to equal amounts of 1-butene and 2-butene (Benson and O'Neal, "Unimolecular Reactions", NSRDS-NBS-21, U.S. Government Printing Office, Washington, DC, 20402). We have neglected the small amounts of isobutene that are also formed. We have carried out extensive RRKM calculations in order to obtain some idea of the magnitude. The general conclusion is that at pressures in the 1 to 10 atmosphere range the methylcyclopropane will not survive under combustion conditions except at the lowest temperatures. Under such conditions we do not expect significant concentrations of ${}^1CH_2$. Butene-1 will also decompose to form allyl and methyl. On the other hand isobutene and butene-2 will be stabilized except at the highest temperatures. Under such conditions we expect that propene concentrations will be drastically reduced. Thus for the present purposes we recommend,

$k_a = k_1 = 5\times10^{-11}$cm³molecule⁻¹s⁻¹
$k_b = 0.5\times k_{2+3+4+5} + k_{3'+4'} =$ 8.7×10^{-11} cm³molecule⁻¹s⁻¹
$k_c = 0.5\times k_2 +_{3+4+5} + k_{5'+6'} =$ 7.2×10^{-11} cm³molecule⁻¹s⁻¹
$k_d = k_{7'+8'} = 0.9\times10^{-11}$ cm³molecule⁻¹s⁻¹

with an uncertainty of a factor of 5.

References

Krzyanowski, S. and Cvetanovic, R. J., "Relative Rates of Reaction of Olefins with the Ground and the First Excited Electronic States of Methylene" Can. J. Chem., **45**, 665, (1967)

Wing Tsang
March, 1990

46,26 $C_3H_6 + {}^3CH_2 \rightarrow {}^1CH_2 + C_3H_6$ (a)
$\rightarrow C_3H_5 + CH_3$ (b)
$\rightarrow C_3H_5 + CH_3$ (c)
$\rightarrow 2\text{-}C_4H_8$ (d)

	Conditions		Reaction rate constant	Uncertainty
Reaction/Reference	T range/K	[M] range/cm^3	k/cm^{3}molecule^{-1}s^{-1}	
Krzyanowski and Cvetanovic (1966), also review	296.5 K	$1-2\times10^{19}$ olefins 9% ketene mercury photosensitized decomposition of ketene	$k_{total}/k(C_2H_4 + {}^3CH_2) = 1$	
Recommendations			$k_a = 2\times10^{-11}\exp(-4480/T)$ $k_b = 1.2\times10^{-12}\exp(-3116/T)$ $k_c = 2.7\times10^{-12}\exp(-2660/T)$ $k_d = 2.7\times10^{-12}\exp(-2660/T)$	1.5 3 5 5

Comments

There is a plethora of possible reaction channels for this process. The more important of these are as follows,

$C_3H_6 + {}^3CH_2 \rightarrow {}^1CH_2 + C_3H_6$ (1)
$\rightarrow c\text{-}C_3H_5CH_3$ (2)
$\rightarrow 1\text{-}C_4H_8$ (3)
$\rightarrow 2\text{-}C_4H_8$ (4)
$\rightarrow C_3H_5 + CH_3$ (5)
$\rightarrow H + C_4H_7$ (6)
$\rightarrow C_3H_5 + CH_3$ (7)

Reactions 3–6 are the consequence of methylcyclopropane formation (2). Reaction (7) represents the abstraction of the allylic hydrogen while reaction (5) is the consequence of the decomposition of hot butene-1. These represent the true elementary reactions. We have expressed the results in terms of a-d in order to reduce the number of rate expressions. The abstraction of vinylic hydrogens should be much slower and will be ignored. Our recommendations for $k_{2+3+4+5+6}$ are based on a combination of the measurements of Krzyanowski and Cvetanovic and the direct determinations of Bohland *et al.* (Ber. Bunsenges. Phys. Chem. **90**, 468, 1986) for the reaction of ${}^3CH_2$ with ethylene. This leads to

$$k_{2+3+4+5+6} = 5.3\times10^{-12}\exp(-2660/T)\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}.$$

with an uncertainty of a factor of 2. At room temperature the data of Kryanowski and Cvetanovic give no indication of contributions from an abstraction process. This then sets an upper limit for possible rate constants at room temperature. Our estimated rate expression is based on the assumption that rate expressions for triplet methylene abstraction of hydrogen will track similar behavior of the isolectronic O-atom. Specifically, we assume that for allylic abstraction

$$k({}^3CH_2 + C_3H_6) = k(O + C_3H_6)*k({}_3CH_2 + C_3H_8)/k(O + C_3H_8),$$

where we make use of the recommended expressions (46,5 and 40,5) and the measurements of Dobe *et al.*. (Ber. Bunsenges. Phys. Chem., **89**, 432, 1985). This leads to the expression;

$$k_7 = 1.2\times10^{-12}\exp(-3116/T)\ \text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$$

with an uncertainty of a factor of 3. At room temperature this is a factor of 20 smaller than the rate constant for addition. For the conversion of ${}^3CH_2$ to ${}^1CH_2$ we use the value for the reverse determined by Bohland (Ber. Bunsenges. Phys. Chem., **89**, 1013, 1985) with propane as the deactivator and through the equilibrium constant arrive at

$$k_1 = 2\times10^{-11}\exp(-4480/T)\ \text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$$

with an uncertainty of a factor of 1.5

The distribution of products from reactions 2 to 6 is dependent upon the temperature and pressure since the reactions go through a common hot methylcylopropane intermediate. From the data on methylcylopropane decomposition Benson and O'Neal, "Unimolecular Reactions", NSRDS-NBS-21, U.S. Government Printing

Office, Washington, DC, 20402) give identical rate expressions for 1-butene and 2-butene formation. Thus $k_{2+3}=k_{4+5}$. There is also a small contribution from an isobutene formation channel. This will be ignored in the present analysis. The hot butenes that are formed can further decompose to form allyl and methyl, and butenyl and H-atom. Ignoring the effect of intersystem crossing on the specific energy of the molecule we have carried out extensive RRKM calculations in order to gauge the magnitude of the branching ratio. For reactions under usual combustion conditions the general mechanism approximates the $^1CH_2$ + C_3H_6 situation. The 38 kJ/mol decrease in excess energy is apparently not sufficient to stabilize the methylcyclopropane or butene-1. Very little butene-2 is destroyed. On this basis we recommend,

$$k_a=k_1=2\times10^{-11}\exp(-4480/T)\ \mathrm{cm^3molecule^{-1}s^{-1}}$$
$$k_b=k_7=1.2\times10^{-12}\exp(-3116/T)\ \mathrm{cm^3molecule^{-1}s^{-1}}$$
$$k_c=0.5\times k_{2+3+4+5+6}=2.7\times10^{-12}\exp(-2660/T)\mathrm{cm^3molecule^{-1}s^{-1}}.$$
$$k_d=0.5\times k_{2+3+4+5+6}=2.7\times10^{-12}\exp(-2660/T)\mathrm{cm^3molecule^{-1}s^{-1}}.$$

with uncertainty factors of 1.5, 3, 5 and 5 respectively.

References

Krzyanowski, S. and Cvetanovic, R. J., "Relative Rates of Reaction of Olefins with the Ground and the First Excited Electronic States of Methylene" Can. J. Chem., **45**, 665, (1967).

Wing Tsang
March, 1990

46,39 C_3H_6 + CH_2OH → C_3H_5 + CH_3OH (a)
→ *n*-C_3H_7 + HCHO (b)
→ *i*-C_3H_7 + HCHO (c)

	Conditions		Reaction rate constant	Uncertainty
Reaction/Reference	T range/K	[M] range/cm^3	k/cm^{3}molecule^{-1}s^{-1}	
Recommendations			$k_a=1\times10^{-22}T^{2.95}\exp(-6033/T)$	10
			$k_b=2\times10^{-14}\exp(-3273/T)\times$ $[\exp(-2500/T)/(1+\exp(-2500/T))]$	10
			$k_c=2\times10^{-14}\exp(-4000/T)\times$ $[\exp(-1700/T)/(1+\exp(-1700/T))]$	10

Comments

There are no data on the kinetics of these processes. We recommend for the abstraction of allylic hydrogens a rate expression that is similar to that for CH_2OH atack on the secondary hydrogens of propane. Reactions b and c are composite reactions that begin with addition to the double bond. At combustion temperatures the newly formed radical will readily decompose. However, the possibility of a 1,4 hydrogen shift will lead to new radicals. Their decomposition products are listed above. In the absence of data we have assummed that the branching will be controlled by the differences in bond energies. The addition rate constant at the terminal position is assummed to be one-half that of the rate of *n*-propyl addition to ethylene (41,18), while the activation energy for addition at the non-terminal position is taken to be 7 kJ/mol higher. This leads to the following rate expressions;

$$k_a = 1\times10^{-22}T^{2.95}\exp(-6033/T)\ \mathrm{cm^3molecule^{-1}s^{-1}}$$
$$k_b = 2\times10^{-14}\exp(-3500/T)\times$$
$$[\exp(-2500/T)/(1+\exp(-2500/T))]\ \mathrm{cm^3molecule^{-1}s^{-1}}$$
$$k_c = 2\times10^{-14}\exp(-4200/T)\times$$
$$[\exp(-1700/T)/(1+\exp(-1700/T))]\ \mathrm{cm^3molecule^{-1}s^{-1}}$$

The uncertainties are factors of 10.

Wing Tsang
June, 1988

46,41 $C_3H_6+n\text{-}C_3H_7 \rightarrow C_3H_5(\text{allyl}) + C_3H_8$ (a)
$\rightarrow 2\text{-}C_2H_4 + C_2H_5$ (b)
$\rightarrow 1\text{-}C_4H_8 + C_2H_5$ (c)
$\rightarrow 1\text{-}C_5H_{10} + CH_3$ (d)

	Conditions		Reaction rate constant	Uncertainty
Reaction/Reference	T range/K	[M] range/cm^3	k/cm^{3}molecule^{-1}s^{-1}	
Recommendations			$k_a=3.7\times10^{-24}T^{3.5}\exp(-3340/T)$	3
			$k_{b+c+d}=1.7\times10^{-13}\exp(-3625/T)$	3
			$k_b/k_{b+c+d}=1/(1+1.33\exp(1000/T))$	3
			$k_c+{}_d/k_{b+c+d}=1/(2+1.5\exp(-1000/T))$	3
			$k_c/k_d = \exp(+1000/T)$	3

Comments

There are no data on the rate constants for these processes. We estimate that the rate constant for the abstraction of the allylic hydrogen will be very similar to that for ethyl radical attack. This leads to the expression

$$k_a=3.7\times10^{-24}T^{3.5}\exp(-3340/T)\ \text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$$

with an uncertainty of a factor of 3.

Addition at the terminal position will lead to the formation of 2-hexyl radical. 1–4 and 1–5 hydrogen migration will lead to 1-hexyl and 3-hexyl formation. These decomposition products are those given for products in channels b-d. We estimate on the basis of the general trends for such processes (Kerr and Parsonage, "Evaluated Kinetic Data on Gas Phase Addition Reactions: Reactions of Atoms and Radical with Alkenes, Alkynes and Aromatic Compounds" Butterworths, London, 1972),

$$k_{b+c+d}=1.7\times10^{-13}\exp(-3625/T)\ \text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$$

with an uncertainty of a factor of 3. This is the same expression as assigned for ethyl radical addition. Assuming rapid isomerization and that the C−H bond energies are the sole determining factor for the branching ratios we obtain

$$k_b/k_{b+c+d}=1/(1+1.333\exp(1000/T))$$
$$k_c+k_d/k_{b+c+d}=1/(2+1.5\exp(-1000/T))$$
$$k_c/k_d = \exp(+1000/T)$$

with an uncertainty of a factor of 3. Non-terminal addition should be slower.

W. Tsang
September, 1988

46,42 $C_3H_6+i\text{-}C_3H_7 \rightarrow C_3H_5+C_3H_8$ (a)
$\rightarrow C_3H_6+n\text{-}C_3H_7$ (b)
$\rightarrow C_2H_4+i\text{-}C_4H_9$ (c)
$\rightarrow i\text{-}C_4H_8+C_2H_5$ (d)

	Conditions		Reaction rate constant	Uncertainty
Reaction/Reference	T range/K	[M] range/cm^3	k/cm^{3}molecule^{-1}s^{-1}	
Szirovicza and Marta(1976)	494–580	$1.3-2.1\times10^{18}$ C_3H_6 $0.6-1.8\times10^{17}$ Azo-isopropane thermolysis	$k_a=5.3\times10^{-15}\exp(-3637/T)$	3
Recommendations			$k_a=1.1\times10^{-25}T^4\exp(-4059/T)$	3
			$k_{b+c+d}=2.2\times10^{-14}\exp(-3110/T)$	3
			$k_b/k_{b+c+d} = 1.13\exp(-1437/T)$	>3
			$k_c/k_{b+c+d} = 0.57\exp(-1437/T)$	>3
			$k_d/k_{b+c+d} = 0.18\exp(562/T)$	>3

Comments

The data of Szirovicza and Marta have been converted to that given here through the use of the recommmended rate expression for isopropyl radical combination (42,42). The experimental points are widely scattered and the A-factor seems anomolously low. We have assummed that their rate constants are correct and derived the expression,

$$k_a = 1.1\times10^{-25}T^4\exp(-4059/T)\ \text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$$

so as to be compatible, through the equilibrium constant with the general form of the reverse allyl + isopropane rate expression (47,40b). The estimated uncertainty is a factor of 3.

From the tabulated data on alkyl radical addition to olefins, (Kerr and Parsonage, "Evaluated Kinetic Data on Gas Phase Addition Reactions: Reactions of Atoms and Radical with Alkenes, Alkynes and Aromatic Compounds" Butterworths, London, 1972), we deduce the following rate expression for terminal addition,

$$k_{b+c+d} = 2.2\times10^{-14}\exp(-3110/T)\ \text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$$

leading to the formation of 4-methylpentyl-2 radical. If we assume that under combustion conditions it can readily decompose or isomerize through 1–4 and 1–5 hydrogen migration, then as a rough estimate we recommend purely on the basis of bond strength

$$k_b/k_{b+c+d} = 1.13\exp(-1437/T)$$
$$k_c/k_{b+c+d} = 0.57\exp(-1437/T)$$
$$k_d/k_{b+c+d} = 0.18\exp(562/T)$$

The uncertainties are greater than a factor of 3. We assume that non-terminal addition will be unimportant.

References

Szirovicza, L. and Marta, F., "Some Reactions of the Isopropyl Radical", Int. J. of Chem. Kin., **8**, 897, (1976).

W. Tsang
October, 1988

46,44 $C_3H_6+t\text{-}C_4H_9 \rightarrow C_3H_5(\text{allyl})+i\text{-}C_4H_{10}$ **(a)**
$\rightarrow C_2H_4+i\text{-}C_4H_8+CH_3$ **(b)**

Reaction/Reference	Conditions T range/K	 [M] range/cm^3	Reaction rate constant k/cm^{3}molecule^{-1}s^{-1}	Uncertainty
Log K_p(a) = $-0.1813+5.195\times10^2/T+5.000\times10^5/T^2-5.913\times10^7/T^3$				
Recommendations			$k_a=4.9\times10^{-29}T^{4.9}\exp(-4005/T)$	6
			$k_{\text{terminal}}=5.1\times10^{-15}\exp(-2962/T)$	10
			$k_b/k_{\text{terminal}}<1/(1+0.16\exp(1000/T))$	

Comments

There are no data on the rate constants for these processes. From our estimated rate expression for abstraction of a tertiary hydrogen by allyl radical (47,43) we obtain through the equilibrium constant the following rate expression

$$k_a = 4.9\times10^{-29}T^{4.9}\exp(-4005/T)\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$$

At 600 K this is about an order of magnitude smaller than the recommended rate expression for isopropyl attack on the allylic hydrogen in propene. We assign an uncertainty of a factor of 6.

T-butyl addition at the terminal position can lead through 1–4 and 1–5 hydrogen migration to new radicals whose decomposition products are given in (b). From the summary of data on alkyl radical addition to olefins, (Kerr and Parsonage, "Evaluated Kinetic Data on Gas Phase Addition Reactions: Reactions of Atoms and Radical with Alkenes, Alkynes and Aromatic Compounds" Butterworths, London, 1972), we deduce the following rate expression for terminal addition,

$$k_{\text{terminal}}=5.1\times10^{-15}\exp(-2962/T)\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$$

At combustion temperatures the reaction will be mostly reversed. However, for rapid radical isomerization and if the relative concentration of alkyl radicals are dependent only on the C—H bond energies of the parent 2,2-dimethylpentane, we then deduce

$$k_b/k_{\text{terminal}}=1/(4+0.67\exp(1000/T))$$

as a maximum value for k_b. The uncertainty is a factor of 10. Note that there cannot be any contributions from non-terminal addition, since the reaction is totally reversed.

W. Tsang
June, 1988

46,45 $C_3H_6 + i\text{-}C_4H_9$ $\rightarrow$ C_3H_5(allyl)$+i\text{-}C_4H_{10}$ (a)
$\rightarrow$ $i\text{-}C_4H_8 + n\text{-}C_3H_7$ (b)
$\rightarrow$ $C_3H_6 + C_2H_4 + C_2H_5$ (c)
$\rightarrow$ 2-$C_2H_4 + i\text{-}C_3H_7$ (d)
$\rightarrow$ 3-methylbutene-1 + C_2H_5 (e)
$\rightarrow$ C_4H_8-1 + $i\text{-}C_3H_7$ (f)

	Conditions		Reaction rate constant	Uncertainty
Reaction/Reference	T range/K	[M] range/cm^3	k/cm^{3}molecule^{-1}s^{-1}	
Recommendations:			$k_a = 3.7\times10^{-24}T^{3.5}\exp(-3340/T)$	3
			$k_{terminal} = 1.7\times10^{-13}\exp(-3625/T)$	3
			$k_b = k_{total}$/total	5
			$k_c = k_{terminal}\times 6\exp(-2000$/total	5
			$k_d = k_{terminal}\times 3\exp(-2000)$/total	5
			$k_e = k_{terminal}\times 2\exp(-1000/T)$/total	5
			$k_f = k_{terminal}\times 2\exp(-1000/T)$/total	5
			where total $= 1 + 6\exp(-1000/T) + 9\exp(-2000/T)$	

Comments

There are no measurements on the rate constants for these reactions. They should however be very similar to n-propyl attack on propene (46,41). Therefore,

$$k_a = 3.7\times10^{-24}T^{3.5}\exp(-3340/T)\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$$
$$k_{terminal} = 1.7\times10^{-13}\exp(-3625/T)\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$$

where $k_{terminal}$ is the rate constant for isobutyl radical addition to the terminal position in propene and the uncertainties are a factor of 3. Under combustion connditions alkyl radicals are unstable. However the possibility of 1–4 and 1–5 hydrogen migration will lead to all the possible alkyl radicals. This will lead to reaction channels b-f. Assumming that the contribution from the various channels are solely dependent on the C–H bond strength in 5-methylpentane, leads to the following values for the branching ratios.

$$k_b = k_{terminal}\text{/total}$$
$$k_c = k_{terminal}\times 6\exp(-2000/T)\text{total}$$
$$k_d = k_{terminal}\times 3\exp(-2000/T)\text{/total}$$
$$k_e = k_{terminal}\times 2\exp(-1000/T)\text{/total}$$
$$k_f = k_{terminal}\times 2\exp(-1000/T)\text{/total}$$
$$\text{where total} = 1 + 6\exp(-1000/T) + 9\exp(-2000/T)$$

where the uncertainties are factors of 3,3,5,5,5,5 and 5 respectively and non-terminal addition is considered to be unimportant.

W. Tsang
June, 1988

46,46 $C_3H_6 + C_3H_6$ $\rightarrow$ 1-hexene (a)
$\rightarrow$ 4-methylpentene-1 (b)
$\rightarrow$ $C_3H_5 + n\text{-}C_3H_7$ (c)
$\rightarrow$ $C_3H_5 + i\text{-}C_3H_7$ (d)

	Conditions		Reaction rate constant	Uncertainty
Reaction/Reference	T range/K	[M] range/cm^3	k/cm^{3}molecule^{-1}s^{-1}	
Log K_p(a) $= -6.671 + 2.975\times10^3/T + 4.946\times10^5/T^2 - 5.961\times10^7/T_3$				
Log K_p(b) $= -7.512 + 3.812\times10^3/T + 1.841\times10^5/T^2 - 9.509\times10^6/T^3$				
Log K_p(c) $= 1.254 - 1.244\times10^4/T + 1.646\times10^5/T^2 - 1.894\times10^7/T^3$				
Log K_p(d) $= 0.8617 - 1.168\times10^4/T + 4.825\times10^4/T^2 - 6.886\times10^6/T^3$				
Recommendation			$k_a = 2.1\times10^{-22}T^{2.5}\exp(-18463/T)$	1.5
			$k_b = 2.8\times10^{-21}T^{2.1}\exp(-18114/T)$	1.5
			$k_c = 4.2\times10^{-10}\exp(-27767/T)$	2.5
			$k_d = 8.1\times10^{-11}\exp(-26323/T)$	2.5

Comments

There are no data on the rate constants for these processes. Our recommendations for (a) and (b) are based on the rate expression for the reverse retro-ene reactions. There is a direct measurement for (– a) (W. Tsang, Int'l J. Chem. Kin., **10**, 1119, (1978)) and from similar data a rate expression for -b can be readily estimated. Since the thermodynamics are well established, this leads to the recommended rate expressions:

$$k_a = 2.1\times10^{-22}T^{2.5}\exp(-18463/T)\ \text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$$
$$k_b = 2.8\times10^{-21}T^{2.1}\exp(-18114/T)\ \text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$$

with an uncertainty of a factor of 1.5. Reactions (c) and (d) are determined on the basis of our recommendations for the rate expressions of the reverse reaction (47,41) and (47,42). Here again the thermodynamics are well established and through the equilibrium constant we find:

$$k_c = 4.2\times10^{-10}\exp(-27767/T)\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$$
$$k_d = 8.1\times10^{-11}\exp(-26323/T)\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$$

with an estimated uncertainty of a factor of 2.5. It should be noted that none of these reactions are likely to be of importance under combustion conditions. However at high concentrations under pyrolysis conditions (c) and (d) may contribute to initiation.

W. Tsang
September, 1988

47,1 $C_3H_5 \rightarrow C_3H_4 + H$

	Conditions		Reaction rate constant	Uncertainty
Reference	T range/K	[M] range/cm^3	k/cm^{3}molecule^{-1}s^{-1}	
$\text{Log } K_p = 6.041-1.318\times10^4/T+1.019\times10^5/T^2-1.258\times10^6/T^3$				
Recommendations	500–2500	infinite	$1.4\times10^{13}\exp(-30192/T)$ $\text{Log }(k(N_2,1.0)/k_\infty)=$ $-0.8103+2.0134\times10^{-3}T$ $-1.4016\times10^{-6}T^2+2.0671\times10^{-10}T^3$	5

Comments

There have been no measurements on the rate constants for this reaction. We have based our recommendations on the rate expressions determined by Wagner and Zellner (Ber. Bunsenges. Phys. Chem., **76**, 518, 1972) for the reverse process and the recommended thermodynamics of the allyl radical. This leads to the high pressure rate expression.

$$k(C_3H_5 \rightarrow C_3H_4 + H) = 1.4\times10^{13}\exp(-30192/T)\ \text{s}^{-1}$$

The A-factor is in the expected range for a radical decomposition process. The uncertainties in the heat of formation of allyl radical are probably the main source of possible errors at the lower temperature. Fortunately allyl is stable under low temperature conditions. At higher temperatures the chief source of uncertainty arise from extrapolation.

The results of fall-off calculations can be found in Tables 1 and 2.

TABLE 1. Log (k/k_∞) for allyl decomposition as a function of temperature and pressure assuming strong collisions

T(K)	500	700	900	1100	1300	1500	1700	1900	2100	2300	2500
Log(density)											
16	–0.01	–0.05	–0.14	–0.28	–0.45	–0.65	–0.86	–1.07	–1.29	–1.50	–1.71
16.5		–0.02	–0.07	–0.16	–0.28	–0.43	–0.60	–0.78	–0.97	–1.15	–1.34
17		–0.01	–0.03	–0.08	–0.16	–0.27	–0.40	–0.54	–0.69	–0.84	–1.00
17.5			–0.01	–0.04	–0.08	–0.15	–0.24	–0.34	–0.45	–0.58	–0.70
18				–0.01	–0.04	–0.07	–0.13	–0.19	–0.27	–0.36	–0.46
18.5				–0.01	–0.01	–0.03	–0.06	–0.10	–0.15	–0.21	–0.27
19					–0.01	–0.01	–0.02	–0.04	–0.07	–0.10	–0.14
19.5							–0.01	–0.02	–0.03	–0.04	–0.06
20								–0.01	–0.01	–0.02	–0.02
20.5										–0.01	–0.01
21											

TABLE 2. Collision efficiency as a function of temperature and step size down for allyl decomposition

	150	300	600	1200	2400
Temp(K)					
500	6.3×10^{-2}	1.6×10^{-1}	3.3×10^{-1}	5.3×10^{-1}	7.1×10^{-1}
700	3.3×10^{-2}	9.5×10^{-2}	2.2×10^{-1}	4.1×10^{-1}	6.1×10^{-1}
900	1.9×10^{-2}	5.8×10^{-2}	1.5×10^{-1}	3.1×10^{-1}	5.1×10^{-1}
1100	1.1×10^{-2}	3.6×10^{-2}	1.0×10^{-1}	2.4×10^{-1}	4.3×10^{-1}
1300	6.9×10^{-3}	2.4×10^{-2}	7.1×10^{-2}	1.8×10^{-1}	3.5×10^{-1}
1500	4.4×10^{-3}	1.6×10^{-2}	4.9×10^{-2}	1.3×10^{-1}	2.9×10^{-1}
1700	3.0×10^{-3}	1.1×10^{-2}	3.6×10^{-2}	1.0×10^{-1}	2.4×10^{-1}
1900	2.3×10^{-3}	8.3×10^{-3}	$2.8\times10-2$	8.4×10^{-2}	2.1×10^{-1}
2100	1.9×10^{-3}	6.9×10^{-3}	2.4×10^{-2}	7.4×10^{-2}	1.9×10^{-1}
2300	1.7×10^{-3}	6.2×10^{-3}	2.2×10^{-2}	7.0×10^{-2}	1.9×10^{-1}
2500	1.6×10^{-3}	6.0×10^{-3}	2.1×10^{-2}	6.9×10^{-2}	1.9×10^{-1}

Comments

We recommend the following expressions for fall off behavior at 0.1, 1.0 and 10 atm. over the temperature range 700–2500 K with N_2 and allyl radical itself at the third body. They are based on the assumption that the step size down for N_2 and allyl are of 500 cm^{-1} and 1000 cm^{-1} respectively. Below 700 K at these pressures reaction are at the high pressure limit.

$$\mathrm{Log}\ (k(N_2,0.1)/k_\infty) = -1.0619+2.9744\times10^{-3}T-2.4031\times10^{-6}T^2+4.2137\times10^{-10}T^3$$

$$\mathrm{Log}\ (k(N_2,1.0)/k_\infty) = -0.8103+2.0134\times10^{-3}T-1.4016\times10^{-6}T^2+2.0671\times10^{-10}T^3$$

$$\mathrm{Log}\ (k(N_2,10)/k_\infty) = -0.2972+6.4524\times10^{-4}T-3.4447\times10^{-7}T^2+9.6986\times10^{-12}T^3$$

$$\mathrm{Log}\ (k(C_3H_5,0.1)/k_\infty) = -0.9042+2.3794\times10^{-3}T-1.7870\times10^{-6}T^{2+}2.9098\times10^{-10}T^3$$

$$\mathrm{Log}\ (k(C_3H_5,1.0)/k_\infty) = -0.4877+1.1460\times10^{-3}T-7.2581\times10^{-7}T^2+8.0570\times10^{-11}T^3$$

$$\mathrm{Log}\ (k(C_3H_5,10)/k_\infty) = -0.0821+1.3496\times10^{-4}T-9.0797\times10^{-9}T^2-3.7830\times10^{-11}T^3$$

Note that in comparison to the alkyl radicals, allyl is much more stable and therefore must play a much more important role in many high temperature processes. We estimate the overall uncertainty as a factor of 5.

Wing Tsang
August, 1988

47,2 $C_3H_5(allyl)+H_2 \rightarrow C_3H_6+H$

Conditions			Reaction rate constant	Uncertainty
Reference	T range/K	[M] range/cm^3	$k/cm^3molecule^{-1}s^{-1}$	
$Log_{10}K_p = -0.6358-3.509\times10^3/T-2.187\times10^4/T^2+1.448\times10^6/T^3$				
Recommendations			$1.8\times10^{-19}T^{2.38}\exp(-9557/T)$	5 at 300 2 at 1100 K

Comments

There are no measurements on the rate constants for this reaction. We have used the rate expression for the reverse process

$$k(C_3H_6+H \rightarrow C_3H_5+H_2)=2.87\times10^{-19}(T)^{2.5}\exp(-1254/T)\ (46,4)$$

and the thermodynamics and obtained

$$k(C_3H_5(allyl)+H_2 \rightarrow C_3H_6+H) = 1.8\times10^{-19}T^{2.38}\exp(-9557/T)cm^3molecule^{-1}s^{-1}$$

with an uncertainty of a factor of 5 at room temperature and decreasing to a factor of 2 at 1100 K and above. Our recommendations are in excellent accord with the experimental results of Collongues *et al.* (Int. J. Chem. Kin., **15**, 5, 1983) who find at 773 K a rate expression of

$$2.1\times10^{-11}\exp(-12236/T)cm^3molecule^{-1}s^{-1}$$

or $2.8\times10^{-18}cm^3molecule^{-1}s^{-1}$ for the process

$$2-C_4H_7+H_2 \rightarrow H+2-C_4H_8.$$

This can be compared with our value of $5.7\times10^{-18}cm^3molecule^{-1}s^{-1}$ at the same temperature.

W. Tsang,
October ,1988

47,3 C_3H_5(allyl)+O_2 → $C_3H_5O_2$ (a)
→ C_3H_4 + HO_2 (b)

	Conditions		Reaction rate constant	Uncertainty
Reference	T range/K	[M] range/cm^3	k/cm^{3}molecule^{-1}s^{-1}	
Slagle and Gutman(1986)	352–800	6×10^{16} He 3×10^{13} 1,5 hexadiene 3×10^{15} O_2 193 nm photolysis ms detection	$<1.1\times10^{-16}$ at 800 overall	
Morgan *et al.* (1982)	382–673	1×10^{18} Ar $3-4\times10^{15}$ 1,5 Hexadiene $5-14\times10^{16}$ O_2 193 nm photolysis allyl radical detection by absorption	$k_a=3.8\times10^{-13}$(383) $k_a=8.5\times10^{-14}$(463) at 1×10^{18}Ar	1.5
Ruiz *et al.* (1981)	348	7.8×10^{16} He 2.8×10^{14} 1,5 Hexadiene $1.2-7.5\times10^{14}$ O_2 193 nm photolysis with ms detection of allyl	$k_a=1.3\times10^{-13}$	2
Recommendations			$k_b<2\times10^{-12}\exp(-6820/T)$	

Comments

The addition reaction is reversed under combustion conditions. This reversal occurs at very low temperatures and has been used by these investigators and others (Slagle, Ratajczak, Heaven, Gutman and Wagner, J. Amer. Chem. Soc. **107**, 1838, 1985) to determine the equilibrium constant for this reaction. The very smnall rate constant determined by Slagel and Gutman is reflection of this phenomenon. The effect of the allylic resonance energy is to reduce the C–O bond strength to 71 kJ/mol. The general trend of the results of Morgan *et al.* is indicative of the measured rate constants being in the fall-off region. We have not carried out RRKM calculations to cover all temperature and pressure ranges because of the reversal of the reaction at low temperatures.

For higher temperatures, there is uncertainty in the importance of the disproportionation reaction to form HO_2 and allene. This is endothermic by approximately 30 kJ/mol and contrasts with the situation with alkyl radicals where the reaction is exothermic by about 69 kJ/mol. Morgan *et al.* claim there is some evidence for this reaction at temperatures above 461 K. The difference between this and the results of Slagle and Gutman may be due to the higher O_2 concentration in the experiments of Morgan *et al.* For the present purposes we set the following expression as an upper limit for the disproportionation reaction;

$$k_b < 2\times10^{-12}\exp(-6820/T)\ \mathrm{cm^3molecule^{-1}s^{-1}}$$

We are also assumming that there is no contribution from a complex rearrangement of the type observed by Slagle and Gutman for the propargyl radical. In general, we suspect that these reactions will not be of major significance in most combustion situations.

References

Morgan, C. A., Pilling, M. J., Tulloch, J. M., Ruiz, R. P. and Bayes, K. D., "Direct Determination of the Equilibrium Constant and Thermodynamic Parameters for the Reaction $C_3H_5+O_2 \rightleftharpoons C_3H_5O_2$" J. Chem. Soc., Faraday Trans. 2, **78**, 1323, 1982.

Ruiz, R. P., Bayes K. D., Macpherson, M. T. and Pilling, M. J. "Direct Observation of the Equilibrium between Allyl Radicals, O_2, and Allylperoxy Radicals, J. Phys. Chem., **85**, 1622, 1981

Slagle, I and Gutman, D. "Kinetics of the Reaction of C_3H_3 with Molecular O_2 from 293–900K", 21st Symposium on Combustion (International), The Combustion Institute, 875, 1986.

W. Tsang
November, 1988

47,4 $C_3H_5 + H \rightarrow C_3H_6$ (a)
$\rightarrow C_2H_3 + CH_3$ (b)
$\rightarrow C_3H_4 + H_2$ (c)

	Conditions		Reaction rate constant	Uncertainty
Reference	T range/K	[M] range/cm^3	k/cm^{3}molecule^{-1}s^{-1}	
Recommendations			$k_{a+b} = 3.3\times10^{-10}$ $\mathrm{Log}(k_b/k_{b+a},N_2,1.0) =$ $-13.6030 + 2.0026\times10^{-2}T$ $-9.9065\times10^{-6}T^2 + 1.6333\times10^{-9}T^3$	3
			$k_c = 3\times10^{-11}$	3

Comments

There are no data on the mechanisms and rate constants for the reaction of hydrogen atoms with the allyl radical. The predominant process must be combination and we assign a large rate constant of

$$k_{a+b} = 3.3 \times 10^{-10}\ \mathrm{cm^3\ molecule^{-1}s^{-1}}$$

with an uncertainty of a factor of 3. Process b is the result of the chemically activated decomposition of the hot propylene molecule. Its rate constant is pressure and temperature dependent. Assumming a rate constant for methyl and vinyl combination of

$$7\times10^{-10}\ \mathrm{cm^3molecule^{-1}s^{-1}},$$

we have found that k_{a+b} does not have any appreciable pressure dependence. The branching ratios k_b/k_{a+b} on the basis of RRKM calculations and strong collisions can be found in Table 1. Collision efficiencies as a function of temperature and step size down are in Table 2. Within our uncertainties there is no pressure dependence for the overall process. For the disproportionation process we assign the rate constant 3×10^{-11} cm^{3}molecule^{-1}s^{-1} with an uncertainty of a factor of 3.

TABLE 1. Branching ratio, Log (k_b/k_{a+b}), as a result of the combination of allyl and hydrogen Atom as a function of temperature and pressure assuming strong collisions

T(K)	500	700	900	1100	1300	1500	1700	1900	2100	2300	2500
Log(density)											
16	−3.51	−1.97	−1.12	−0.60	−0.30	−0.14	−0.07	−0.03	−0.01	−0.01	
16.5	−3.92	−2.27	−1.34	−0.78	−0.43	−0.23	−0.11	−0.06	−0.03	−0.01	−0.01
17	−4.38	−2.64	−1.61	−0.98	−0.58	−0.34	−0.19	−0.10	−0.05	−0.03	−0.02
17.5	−4.86	−3.05	−1.94	−1.23	−0.78	−0.48	−0.29	−0.17	−0.10	−0.06	−0.03
18	−5.35	−3.50	−2.32	−1.54	−1.02	−0.67	−0.43	−0.27	−0.17	−0.11	−0.07
18.5	−5.85	−3.98	−2.74	−1.90	−1.32	−0.91	−0.62	−0.42	−0.28	−0.18	−0.12
19	−6.35	−4.47	−3.21	−2.31	−1.67	−1.20	−0.86	−0.61	−0.43	−0.31	−0.22
19.5	6.85	−4.97	−3.69	−2.76	−2.07	−1.55	−1.16	−0.87	−0.65	−0.48	−0.36
20	−7.35	−5.47	−4.19	−3.24	−2.52	−1.96	−1.52	−1.18	−0.92	−0.72	−0.57
20.5	−7.85	−5.97	−4.68	−3.73	−3.00	−2.41	−1.94	−1.56	−1.27	−1.03	−0.86
21	−8.35	−6.47	−5.18	−4.23	−3.49	−2.89	−2.40	−2.00	−1.68	−1.42	−1.22

TABLE 2. Collision efficiency as a function of temperature and step size down for the combination of allyl radicals and hydrogen atoms

Step Size (cm^{-1})	150	300	600	1200	2400
Temp(K)					
500	6.5×10^{-2}	1.7×10^{-1}	3.3×10^{-1}	5.4×10^{-1}	7.2×10^{-1}
700	3.5×10^{-2}	1.0×10^{-1}	2.3×10^{-1}	4.2×10^{-1}	6.2×10^{-1}
900	2.1×10^{-2}	6.3×10^{-2}	1.6×10^{-1}	3.3×10^{-1}	5.3×10^{-1}
1100	1.3×10^{-2}	4.1×10^{-2}	1.1×10^{-1}	2.5×10^{-1}	4.5×10^{-1}
1300	7.9×10^{-3}	2.7×10^{-2}	7.9×10^{-2}	1.9×10^{-1}	3.7×10^{-1}
1500	5.1×10^{-3}	1.8×10^{-2}	5.5×10^{-2}	1.5×10^{-1}	3.1×10^{-1}
1700	3.3×10^{-3}	1.2×10^{-2}	3.9×10^{-2}	1.1×10^{-1}	2.4×10^{-1}
1900	2.2×10^{-3}	8.1×10^{-3}	$2.7\times10-2$	8.0×10^{-2}	2.0×10^{-1}
2100	1.5×10^{-3}	5.7×10^{-3}	2.0×10^{-2}	6.0×10^{-2}	1.6×10^{-1}
2300	1.1×10^{-3}	4.1×10^{-3}	1.4×10^{-2}	4.6×10^{-2}	1.3×10^{-1}
2500	8.1×10^{-4}	3.0×10^{-3}	1.1×10^{-2}	3.6×10^{-2}	1.0×10^{-1}

Comments

We recommend the following expressions for branching ratios at 0.1, 1.0 and 10 atm. over the temperature range 700–2500 K with N_2 and propene as the third body. They are based on the assumption that the step size down for N_2 and propene are of 500 cm^{-1} and 1000 cm^{-1} respectively.

$$\mathrm{Log}(k_b/k_b+k_a,\mathrm{N_2},0.1) = -12.1630+1.9262\times10^{-2}T-1.0080\times10^{-5}T^2+1.7341\times10^{-10}T^3$$

$$\mathrm{Log}(k_b/k_b+k_a,\mathrm{N_2},1.0) = -13.6030+2.0026\times10^{-2}T-9.9065\times10^{-6}T^2+1.6333\times10^{-9}T^3$$

$$\mathrm{Log}(k_b/k_b+k_a,\mathrm{N_2},10.1) = -14.5185+1.9332\times10^{-2}T-8.8213\times10^{-6}T^2+1.3663\times10^{-9}T^3$$

$$\mathrm{Log}(k_b/k_b+k_a,\mathrm{C_3H_6},0.1) = -12.5146+1.9128\times10^{-2}T-9.7517\times10^{-6}T^2+1.6462\times10^{-10}T^3$$

$$\mathrm{Log}(k_b/k_b+k_a,\mathrm{C_3H_6},1.0) = -13.7173+1.9226\times10^{-2}T-9.1640\times10^{-6}T^2+5.4465\times10^{-9}T^3$$

$$\mathrm{Log}(k_b/k_b+k_a,\mathrm{C_3H_6},10.0) = -14.4567+1.8128\times10^{-2}T-7.9103\times10^{-6}T^2+1.1884\times10^{-9}T^3$$

Wing Tsang
September, 1988

47,5 C_3H_5(allyl)+O → C_2H_3CHO + H

	Conditions		Reaction rate constant	Uncertainty
Reference	T range/K	[M] range/cm^3	k/$cm^3 molecule^{-1}s^{-1}$	
Recommendations			1.0×10^{-10}	2.5

Comments

There are no data on the mechanisms and rate constants for this reaction. However there can be little doubt that the initial process is addition, forming a hot molecule, followed by ejection of an allylic hydrogen or 1,2 hydrogen migration of the allylic hydrogen to the oxygen (as in the alkyl radicals) followed by the cleavage of the O−H bond. The rate constant for the combination process must be fast and we suggest 1.0 × 10^{-10} $cm^3 molecule^{-1}s^{-1}$ with an uncertainty of a factor of 2.5.

Wing Tsang
September, 1988

47,6 C_3H_5(allyl)+OH → C_3H_4 + H_2O (a)
→ C_3H_5OH (b)
→ C_2H_3CHO + 2H (c)

	Conditions		Reaction rate constant	Uncertainty
Reference	T range/K	[M] range/cm^3	k/$cm^3 molecule^{-1}s^{-1}$	
Recommendations			$k_a=1\times10^{-11}$	3
			$k_{b+c}=2.5\times10^{-11}$	2
			$\mathrm{Log}\ (k_{b+c}/k_{b+c\infty},\mathrm{N_2},1.0) =$ $-0.6720+1.9954\times10^{-3}\mathrm{T}$ $-1.6251\times10^{-6}T^2+3.2547\times10^{-10}T^3$ $\mathrm{Log}\ (k_c/k_{b+c},\mathrm{N_2},1.0) =$ $-13.2116+1.6774\times10^{-2}\mathrm{T}$ $-7.4344\times10^{-6}T^2+1.1378\times10^{-9}T^3$	

Comments

There have been no measurements on the rate constants for these reactions. Reaction (a) is a disproportionation process. From comparable reactions we suggest a rate constant of 1×10^{-11} $cm^3 molecule^{-1}s^{-1}$ with an uncertainty of a factor of 3. We estimate the rate constant for addition as 2.5×10^{-11} $cm^3 molecule^{-1}s^{-1}$ with an uncertainty of a factor of 2. Since OH substitution weakens the alpha hydrogen bond, we believe that the weakly endothermic process leading to hydrogen ejection and ultimately the formation of acrolein and another hydrogen atom, reaction (c) can make a contribution. The result of RRKM calculations can be found in Tables 1–3. Note, from Table 1 that fall-off effects are unimportant except at the highest temperatures.

TABLE 1. Log ($k_{b+c}/k_{b+c\infty}$) for combination of allyl and hydroxyl radical as a function of temperature and pressure assuming strong collisions

T(K)	500	700	900	1100	1300	1500	1700	1900	2100	2300	2500
Log(density)											
16		−0.01	−0.05	−0.15	−0.30	−0.46	−0.60	−0.69	−0.74	−0.75	−0.74
16.5			−0.02	−0.08	−0.19	−0.33	−0.47	−0.58	−0.66	−0.70	−0.71
17			−0.01	−0.04	−0.11	−0.21	−0.33	−0.45	−0.55	−0.62	−0.66
17.5				−0.02	−0.06	−0.12	−0.21	−0.32	−0.42	−0.51	−0.58
18				−0.01	−0.02	−0.06	−0.12	−0.21	−0.31	−0.39	−0.47
18.5					−0.01	−0.03	−0.06	−0.12	−0.18	−0.26	−0.34
19						−0.01	−0.03	−0.06	−0.10	−0.16	−0.22
19.5							−0.01	−0.03	−0.05	−0.08	−0.12
20								−0.01	−0.02	−0.04	−0.06
20.5									−0.01	−0.01	−0.02
21											−0.01

TABLE 2. Branching ratio, Log (k_c/k_{c+b}), as a result of the combination of allyl and hydroxyl radical as a function of temperature and pressure assuming strong collisions

T(K)	500	700	900	1100	1300	1500	1700	1900	2100	2300	2500
Log(density)											
16	−4.13	−2.71									
−1.85	−1.29	−0.89	−0.57	−0.34	−0.18	−0.09	−0.04	−0.02			
16.5	−4.62	−3.11	−2.15	−1.53	−1.10	−0.76	−0.50	−0.30	−0.17	−0.09	−0.05
17	−5.11	−3.55	−2.50	−1.81	−1.33	−0.97	−0.69	−0.47	−0.30	−0.18	−0.10
17.5	−5.61	−4.02	−2.90	−2.13	−1.60	−1.21	−0.91	−0.66	−0.46	−0.31	−0.20
18	−6.11	−4.51	−3.35	−2.51	−1.92	−1.48	−1.15	−0.88	−0.66	−0.49	−0.35
18.5	−6.60	−5.01	−3.82	−2.94	−2.29	−1.80	−1.42	−1.13	−0.89	−0.70	−0.53
19	−7.10	−5.50	−4.31	−3.41	−2.71	−2.17	−1.75	−1.42	−1.16	−0.94	−0.76
19.5	−7.60	−6.00	−4.81	−3.89	−3.16	−2.59	−2.13	−1.76	−1.47	−1.22	−1.02
20	−8.10	−6.50	−5.31	−4.38	−3.65	−3.05	−2.56	−2.16	−1.83	−1.56	−1.33
20.5	−8.60	−7.00	−5.81	−4.88	−4.14	−3.53	−3.03	−2.60	−2.25	−1.95	−1.70
21	−9.10	−7.50	−6.31	−5.38	−4.64	−4.03	−3.51	−3.08	−2.71	−2.40	−2.13

TABLE 3. Collision efficiency as a function of temperature and step size down for the combination of allyl radicals and hydrogen atoms

Step Size (cm^{-1})	150	300	600	1200	2400
Temp(K)					
500	6.2×10^{-2}	1.6×10^{-1}	3.2×10^{-1}	5.3×10^{-1}	7.1×10^{-1}
700	3.2×10^{-2}	9.2×10^{-2}	2.2×10^{-1}	4.0×10^{-1}	6.0×10^{-1}
900	1.8×10^{-2}	5.6×10^{-2}	1.5×10^{-1}	3.1×10^{-1}	5.1×10^{-1}
1100	1.0×10^{-2}	3.4×10^{-2}	9.7×10^{-2}	2.3×10^{-1}	4.2×10^{-1}
1300	6.1×10^{-3}	2.1×10^{-2}	6.4×10^{-2}	1.6×10^{-1}	3.3×10^{-1}
1500	3.7×10^{-3}	1.3×10^{-2}	4.2×10^{-2}	1.2×10^{-1}	2.6×10^{-1}
1700	2.3×10^{-3}	8.4×10^{-3}	2.8×10^{-2}	8.2×10^{-2}	2.0×10^{-1}
1900	1.5×10^{-3}	5.6×10^{-3}	$1.9\times10-2$	5.9×10^{-2}	1.5×10^{-1}
2100	1.0×10^{-3}	3.9×10^{-3}	1.4×10^{-2}	4.4×10^{-2}	1.2×10^{-1}
2300	7.2×10^{-4}	2.7×10^{-3}	9.8×10^{-3}	3.2×10^{-2}	9.2×10^{-2}
2500	5.2×10^{-4}	2.0×10^{-3}	7.2×10^{-3}	2.4×10^{-2}	7.1×10^{-2}

Comments

Assumming that the step size down is constant at 500 cm^{-1} and 1000 cm^{-1} for N_2 and C_5H_6, respectively, we find for temperatures in excess of 900 K the following relations for the fall off behavior and branching ratio at 0.1, 1, and 10 atm. respectively.

$$\mathrm{Log}\ (k_{b+c}/k_{b+c\infty},n_2,0.1) = -0.7084+2.3524\times10^{-3}T-2.1885\times10^{-6}T^2+4.9789\times10^{-10}T^3$$

$$\mathrm{Log}\ (k_{b+c}/k_{b+c\infty},n_2,1.0) = -0.6720+1.9954\times10^{-3}T-1.6251\times10^{-6}T^2+3.2547\times10^{-10}T^3$$

$$\mathrm{Log}\ (k_{b+c}/k_{b+c\infty},n_2,10.0) = -0.2728+7.1833\times10^{-4}T-4.6565\times10^{-7}T^2+4.5192\times10^{-11}T^3$$

$$\mathrm{Log}\ (k_{b+c}/k_{b+c\infty},c_3h_5oh,0.1) = -0.7260+2.2547\times10^{-3}T-1.9466\times10^{-6}T^2+4.1653\times10^{-10}T^3$$

$$\mathrm{Log}\ (k_{b+c}/k_{b+c\infty},c_3h_5oh,1.0) = -0.4465+1.2594\times10^{-3}T-9.4252710^{-6}T^2+1.5756\times10^{-10}T^3$$

$$\mathrm{Log}\ (k_{b+c}/k_{b+c\infty},c_3h_5oh,10.0) = -0.0542+7.8793\times10^{-5}T-5.3683\times10^{-8}T^2-6.6038\times10^{-11}T^3$$

$$\mathrm{Log}\ (k_c/k_{b+c},n_2,0.1) = -11.8983+1.6290\times10^{-2}T-7.6016\times10^{-6}T^2+1.1993\times10^{-9}T^3$$

$$\mathrm{Log}\ (k_c/k_{b+c},n_2,1.0) = -13.2116+1.6774\times10^{-2}T-7.4344\times10^{-6}T^2+1.1378\times10^{-9}T^3$$

$$\mathrm{Log}\ (k_c/k_{b+c},n_2,10.0) = -14.1976+1.6397\times10^{-2}T-6.7845\times10^{-6}T^2-9.9342\times10^{-10}T^3$$

$$\mathrm{Log}\ (k_c/k_{b+c},c_3h_5oh,0.1) = -12.1910+1.6013\times10^{-2}T-7.2823\times10^{-6}T^2+1.1344\times10^{-9}T^3$$

$$\mathrm{Log}\ (k_c/k_{b+c},c_3h_5oh,1.0) = -13.3858+1.6190\times10^{-2}T-6.9707\times10^{-6}T^2+1.0536\times10^{-9}T^3$$

$$\mathrm{Log}\ (k_c/k_{b+c},c_3h_5oh,10.0) = -14.1977+1.5394\times10^{-2}T-6.0927\times10^{-6}T^2+8.6754\times10^{-9}T^{-3}$$

Wing Tsang
September, 1989

47,7 $C_3H_5(allyl)+HO_2 \rightarrow OH + C_3H_5O \rightarrow C_2H_3CHO(acrolein) + H$

	Conditions		Reaction rate constant	Uncertainty
Reference	T range/K	[M] range/cm^3	$k/cm^3molecule^{-1}s^{-1}$	
Recommendations			1.6×10^{-11}	3

Comments

There are no data on the mechanisms and rate constants for this reaction. There can be little doubt that the reaction involve combination of the two radicals, followed under combustion conditions by the cleavage of the weak O – O bond. We believe that the C_3H_5O radical will rapidly decompose to form acrolein and a hydrogen atom. The recommended rate constant is 1.6×10^{-11} $cm^3molecule^{-1}s^{-1}$ with an uncertainty of a factor of 3.

Wing Tsang
September, 1988

47,8 $C_3H_5(allyl)+H_2O_2 \rightarrow C_3H_6 + HO_2$

	Conditions		Reaction rate constant	Uncertainty
Reference	T range/K	[M] range/cm^3	$k/cm^3molecule^{-1}s^{-1}$	
Log K_p = $-0.4287+5.622\times10^2/T-1.251\times10^5/T^2+1.094\times10^7/T^3$				
Recommendations			$6.5\times10^{-19}T^{2.05}\exp(-6833/T)$	10

Comments

There are no kinetic data on this reaction. We have made our estimate on the basis of the rate expression for the reverse reaction (46,7) and the thermodynamics of the system. This yields;

$$k(C_3H_5(allyl)+H_2O_2 \rightarrow C_3H_6+HO_2) = 6.5\times10^{-19}T^{2.05}\exp(-6833/T)cm^3molecule^{-1}s^{-1}$$

Note that the rate expression for the reverse is an estimate based on the general observed trends of radical abstraction rates from allylic hydrogen. We estimate an uncertainty of a factor of 10.

W. Tsang
August, 1988

47,10 $C_3H_5(allyl)+CH_4 \rightarrow C_3H_6 + CH_3$

Reaction/Reference	Conditions T range/K	 [M] range/cm^3	Reaction rate constant k/cm^{3}molecule^{-1}s^{-1}	Uncertainty
Log $K_p = 8.743-3.696\times10^3/T-5.551\times10^4/T^2+8.597\times10^6/T^3$				
Recommendations			$6.6\times10^{-23}(T)^{3.4}\exp(-11669/T)$	3

Comments

There are no data on the rate constants for this process. From the rate expression for the reverse process (46,16) and the equilibrium constant, we arrive at the rate expression;

$$k(C_3H_5(allyl)+CH_4\rightarrow C_3H_6+CH_3) = 6.6\times10^{-23}(T)^{3.4}\exp(-11669/T)\ cm^3molecule^{-1}s^{-1}$$

We estimate the uncertainty as a factor of 3.

W. Tsang
September, 1988

47,11 $C_3H_5(allyl)+C_2H_6 \rightarrow C_3H_6 + C_2H_5$

Reference	Conditions T range/K	 [M] range/cm^3	Reaction rate constant k/cm^{3}molecule^{-1}s^{-1}	Uncertainty
Log $K_p = 1.191-2.674\times10^3/T-6.058\times10^4/T^2+6.402\times10^6/T^3$				
Recommendations			$3.9\times10^{-22}(T)^{3.3}\exp(-9986/T)$	4

Comments

There are no data on the rate constants for this reaction. From the recommended rate expression of the reverse reaction (46,17) and the thermodynamic properties we derive

$$k(C_3H_5(allyl)+C_2H_6 \rightarrow C_3H_6 + C_2H_5) = 3.9\times10^{-22}(T)^{3.3}\exp(-9986/T)\ cm^3molecule^{-1}s^{-1}$$

We estimate the uncertainty as a factor of 4.

W. Tsang
September, 1988

47,12 C_3H_5 (allyl) + HCHO $\rightarrow C_3H_6$ + CHO

Reaction/Reference	Conditions T range/K	 [M] range/cm^3	Reaction rate constant k/cm^{3}molecule^{-1}s^{-1}	Uncertainty
Log $K_p = 0.6061-121.0/T-4.413\times10^4/T^2+5.359\times10^6/T^3$				
Recommendations			$2.4\times10^{-16}T^{1.8}\exp(-9154/T)$	10

Comments

There are no data on the kinetics of this reaction. We have used the recommendation for the reverse process (46,15) and the thermodynamics to obtain

$$k(C_3H_5+HCHO \rightarrow C_3H_6+CHO) = 2.4\times10^{-16}T^{1.8}\exp(-9154/T)\ cm^3molecule^{-1}s^{-1}$$

The rate expression for the reverse is however only an estimate. We therefore assign an uncertainty of a factor of 10.

Wing Tsang
September, 1988

47,15 C_3H_5(allyl)+HCO → C_3H_6 + CO (a)
→ C_3H_5CHO (b)

Reference	Conditions T range/K	 [M] range/cm^3	Reaction rate constant k/cm^{3}molecule^{-1}s^{-1}	Uncertainty
Recommendations			$k_a = 1 \times 10^{-10}$ $k_b = 2 \times 10^{-11}$	5 2

Comments

There are no data. We assume that the rates and mechanisms will parallel that of the alkyl radicals and therefore suggest that the disproportionation reaction will be the predominant process. The recommended rate expressions are

$k_a = 1 \times 10^{-10}$ cm^{3}molecule^{-1}s^{-1}
$k_b = 2 \times 10^{-11}$ cm^{3}molecule^{-1}s^{-1}

with an uncertainty of a factor of 5 and 2 respectively. Reaction b will under certain conditions be in the fall-off region. Therefore the number given here is an upper limit. However the instability of the HCO radical makes it unlikely that this will be an important process at the higher temperatures where fall-off effects will be most serious. For a rough idea of the magnitude of the fall-off effect use the data for allyl+methyl (47,16).

W. Tsang
August, 1988

47,16 C_3H_5(allyl) + CH_3 → CH_4 + C_3H_4(allene) (a)
→ C_4H_8 (1-butene)(b)

Reaction/Reference	Conditions T range/K	 [M] range/cm^3	Reaction rate constant k/cm^{3}molecule^{-1}s^{-1}	Uncertainty
Recommendations			$k_a = 0.5\times10^{-11}T^{-0.32}\exp(66/T)\mathrm{s}^{-1}$ $k_{b,\infty} = 1.69\times10^{-10}T^{-0.32}\exp(132/T)\mathrm{s}^{-1}$ Log $k_b/k_{b,\infty}(N_2,1.0) = -1.4674$ $+3.5845\times10^{-3}T-2.4575\times10^{-6}T^2$ $+3.7803\times10^{-10}T^3$	3 1.5

Comments

There are no data on the mechanisms and rate constants for the reactions of methyl and allyl. There can only be two distinct channels. For the combination of allyl and methyl we combine the data on methyl radical combination (16,16) with that of allyl radical combination (47,47) and the geometric mean rule and derive

$$k_{b,\infty} = 1.69\times10^{-10}T^{-0.32}\exp(66/T)\ \mathrm{s}^{-1}$$

with an uncertainty of a factor 1.5. For the disproportionation process, from the published data on ethyl + allyl (47,17) we estimate a disproportionation to combination ratio of 0.03. This leads to

$$k_a = 0.5\times10^{-11}T^{-0.32}\exp(132/T)\ \mathrm{s}^{-1}$$

with an uncertainty of a factor of 3. At sufficiently high temperatures the addition process will be in the fall-off region. RRKM calculations lead to the results summarized in Tables 1 and 2.

TABLE 1. Log ($k_b/k_{b,\infty}$) for allyl combination with methyl as a function of temperature and pressure assuming strong collisions

T(K)	500	700	900	1100	1300	1500	1700	1900	2100	2300	2500
Log(density)											
16		−0.01	−0.08	−0.24	−0.47	−0.76	−1.08	−1.41	−1.75	−2.09	−2.41
16.5		−0.01	−0.04	−0.14	−0.31	−0.54	−0.80	−1.09	−1.39	−1.69	−1.99
17			−0.02	−0.07	−0.19	−0.35	−0.56	−0.80	−1.06	−1.32	−1.59
17.5			−0.01	−0.03	−0.10	−0.21	−0.37	−0.55	−0.77	−0.99	−1.22
18				−0.01	−0.05	−0.11	−0.22	−0.36	−0.52	−0.70	−0.89
18.5				−0.01	−0.02	−0.05	−0.12	−0.21	−0.32	−0.46	−0.61
19					−0.01	−0.02	−0.05	−0.11	−0.18	−0.27	−0.38
19.5						−0.01	−0.02	−0.05	−0.09	−0.14	−0.21
20							−0.01	−0.02	−0.04	−0.06	−0.10
20.5								−0.01	−0.01	−0.03	−0.04
21										−0.01	−0.02

TABLE 2. Collision efficiency as a function of temperature and step size down for the combination of methyl and allyl radicals

Step Size	150	300	600	1200	2400
Temp(K)					
500	5.7×10^{-2}	1.5×10^{-1}	3.1×10^{-1}	5.1×10^{-1}	7.0×10^{-1}
700	2.8×10^{-2}	8.2×10^{-2}	2.0×10^{-1}	3.8×10^{-1}	5.8×10^{-1}
900	1.5×10^{-2}	4.6×10^{-2}	1.3×10^{-1}	2.7×10^{-1}	4.7×10^{-1}
1100	7.9×10^{-3}	2.7×10^{-2}	7.9×10^{-2}	1.9×10^{-1}	3.7×10^{-1}
1300	4.3×10^{-3}	1.5×10^{-2}	4.8×10^{-2}	1.3×10^{-1}	2.8×10^{-1}
1500	2.6×10^{-3}	9.5×10^{-3}	3.2×10^{-2}	9.3×10^{-2}	2.2×10^{-1}
1700	1.9×10^{-3}	7.0×10^{-3}	2.4×10^{-2}	7.4×10^{-2}	1.9×10^{-1}
1900	1.6×10^{-3}	6.0×10^{-3}	2.1×10^{-2}	6.7×10^{-2}	1.8×10^{-1}
2100	1.5×10^{-3}	5.7×10^{-3}	2.0×10^{-2}	6.7×10^{-2}	1.9×10^{-1}
2300	1.6×10^{-3}	5.9×10^{-3}	2.1×10^{-2}	7.1×10^{-2}	2.1×10^{-1}
2500	1.7×10^{-3}	6.4×10^{-3}	2.3×10^{-2}	7.8×10^{-2}	2.3×10^{-1}

Comments

We recommend the following expressions for fall off behavior at 0.1, 1.0 and 10 atm. over the temperature range 900–2500 K with N_2 and 1-butene as the third body. They are based on the assumption that the step size down for N_2 and 1-butene are of 500 cm^{-1} and 1000 cm^{-1} respectively. Below 900 K at these pressures the reactions are at the high pressure limit and indeed for most representative combustion situations fall-off effects are small.

$$\text{Log}\ (k(N_2,0.1)/k_\infty) = -2.5566+6.2985\times10^{-3}T-4.5964\times10^{-6}T^2+8.1597\times10^{-10}T^3$$

$$\text{Log}\ (k(N_2,1.0)/k_\infty) = -1.4674+3.5845\times10^{-3}T-2.4575\times10^{-6}T^2+3.7803\times10^{-10}T^3$$

$$\text{Log}\ (k(N_2,10)/k_\infty) = -2.3825+4.5354\times10^{-3}T-2.5848\times10^{-6}T^2-3.8480\times10^{-10}T^3$$

$$\text{Log}\ (k(C_4H_8,0.1)/k_\infty) = -1.6285+4.1440\times10^{-3}T-2.9990\times10^{-6}T^2+4.9611\times10^{-10}T^3$$

$$\text{Log}\ (k(C_4H_8,1.0)/k_\infty) = -0.9720+2.2750\times10^{-3}T-1.4526\times10^{-6}T^2+1.8515\times10^{-10}T^3$$

$$\text{Log}\ (k(C_4H_8,10)/k_\infty) = -0.2860+5.5868\times10^{-4}T-2.1958\times10^{-7}T^2-3.4377\times10^{-11}T^3$$

The overall uncertainty is a factor of 2.

W. Tsang
September, 1988

47,17 $C_3H_5(allyl)+C_2H_5 \rightarrow C_3H_4(allyl)+C_2H_6$ (a)
$\rightarrow C_3H_6 + C_2H_4$ (b)
$\rightarrow 1\text{-}C_5H_{10}$ (c)$\rightarrow C_3H_6 + C_2H_4$ (d)

	Conditions		Reaction rate constant	Uncertainty
Reference	T range/K	[M] range/cm^3	k/cm^{3}molecule^{-1}s^{-1}	
James and Troughton, (1966)	407–448	313nm photolysis of 4.5×10^{17} diethylketone in 4.5×10^{17} diallyl	$k_a/k_{c+d}=0.047$ $k_b/k_{c+d}=0.13$	1.4 1.4
Recommendations			$k_{c+d}=3.3\times10^{-11}\exp(66/T)$ $k_a=1.6\times10^{-12}\exp(66/T)$ $k_b=4.3\times10^{-12}\exp(66/T)$ $\mathrm{Log}\ (k_{c+d}(N_2,1.0)/k_{c+d\infty}) = -1.8581+4.7581\times10^{-3}T -3.5095\times10^{-6}T^2+6.3896\times10^{-10}T^3$ $\mathrm{Log}\ (k_c/(k_{c+d}),N_2,1) = +0.1125-3.3027\times10^{-4}T +3.1937\times10^{-7}T^2-1.0478\times10^{-10}T^3$	1.5 2 2

Comment

The only measurements are those of James and Troughton. They demonstrate that the rate constants for the disproportionation-combination reactions of allyl and ethyl radicals are similar to those for alkyl radicals. Their disproportionation-combination ratios are accepted and will be used to derive rate expressions for disproportionation.

The rate expression for the combination of allyl and ethyl have been deduced that of allyl (47,47) and ethyl (17,17) and the geometric mean rule. This leads to the expressions

$$k_{c+d} = 3.3\times10^{-11}\ \mathrm{Exp}(66/T)\ \mathrm{cm^3molecule^{-1}s^{-1}}$$
$$k_a = 1.6\times10^{-12}\ \mathrm{Exp}(66/T)\ \mathrm{cm^3molecule^{-1}s^{-1}}$$
$$k_b = 4.3\times10^{-12}\ \mathrm{Exp}(66/T)\ \mathrm{cm^3molecule^{-1}s^{-1}}$$

with uncertainties of a factors of 1.5, 2 and 2 respectively.

At higher temperatures the combination process is in the fall-off region and there is also a chemically activated decomposition of the hot pentene-1 to form ethylene and propene. RRKM calculations leading to log $(k_{c+d}/k_{c+d,\infty})$ can be found in Table 1. Table 2 gives the logarithm of the branching ratio for stabilization k_c to the sum of molecular decomposition and stabilization. It can be seen that except at the highest temperatures where ethyl radicals will have very short lifetimes the decomposition channel is unimportant. Thus for most combustion related purposes use of the high pressure rate expressions will be of sufficient accuracy. Table 3 gives collision efficiency for various step sizes down.

TABLE 1. Log $(k_{c+d}/k_{c+d,\infty})$ for allyl combination with ethyl as a function of temperature and pressure assuming strong collisions

T(K)	500	700	900	1100	1300	1500	1700	1900	2100	2300	2500
Log(density)											
16			−0.05	−0.20	−0.45	−0.77	−1.13	−1.47	−1.75	−1.96	−2.10
16.5			−0.02	−0.11	−0.30	−0.56	−0.89	−1.23	−1.54	−1.81	−2.00
17			−0.01	−0.06	−0.18	−0.38	−0.65	−0.96	−1.28	−1.57	−1.82
17.5				−0.03	−0.10	−0.24	−0.45	−0.70	−0.99	−1.28	−1.55
18				−0.01	−0.05	−0.13	−0.28	−0.48	−0.72	−0.97	−1.23
18.5					−0.02	−0.07	−0.16	−0.30	−0.48	−0.69	−0.91
19					−0.01	−0.03	−0.08	−0.17	−0.29	−0.45	−0.62
19.5						−0.01	−0.03	−0.08	−0.16	−0.26	−0.39
20							−0.01	−0.03	−0.07	−0.13	−0.21
20.5								−0.01	−0.03	−0.06	−0.10
21									−0.01	−0.02	−0.04

TABLE 2. Log (k_c/k_{c+d}) for allyl Combination with ethyl to produce 1-pentene(c) and propylene and ethylene(d) as a function of temperature and pressure assuming strong collisions

T(K)	500	700	900	1100	1300	1500	1700	1900	2100	2300	2500
Log(density)											
16			−0.01	−0.02	−0.04	−0.07	−0.12	−0.23	−0.39	−0.61	−0.88
16.5				−0.01	−0.02	−0.03	−0.06	−0.11	−0.19	−0.33	−0.52
17					−0.01	−0.02	−0.03	−0.05	−0.09	−0.16	−0.26
17.5						−0.01	−0.01	−0.02	−0.04	−0.07	−0.12
18							−0.01	−0.01	−0.02	−0.03	−0.05
18.5								−0.01	−0.01	−0.01	−0.02
19										−0.01	−0.01
19.5											
20											
20.5											
21											

TABLE 3. Collision Efficiency as a Function of Temperature and Step Size Down for the Combination of Methyl and Ethyl Radicals

	150	300	600	1200	2400
Temp. (K)					
500	5.2×10^{-2}	1.4×10^{-1}	2.9×10^{-1}	4.9×10^{-1}	6.8×10^{-1}
700	2.4×10^{-2}	7.2×10^{-2}	1.8×10^{-1}	3.5×10^{-1}	5.6×10^{-1}
900	1.1×10^{-2}	3.7×10^{-2}	1.0×10^{-1}	2.4×10^{-1}	4.3×10^{-1}
1100	5.4×10^{-3}	1.9×10^{-2}	5.8×10^{-2}	1.5×10^{-1}	3.1×10^{-1}
1300	2.8×10^{-3}	1.0×10^{-2}	3.4×10^{-2}	9.7×10^{-2}	2.3×10^{-1}
1500	1.8×10^{-3}	6.8×10^{-3}	2.4×10^{-2}	7.3×10^{-2}	1.9×10^{-1}
1700	1.5×10^{-3}	5.8×10^{-3}	2.1×10^{-2}	6.7×10^{-2}	1.9×10^{-1}
1900	1.6×10^{-3}	5.9×10^{-3}	2.1×10^{-2}	7.1×10^{-2}	2.1×10^{-1}
2100	1.8×10^{-3}	6.7×10^{-3}	2.5×10^{-2}	8.3×10^{-2}	2.5×10^{-1}
2300	2.1×10^{-3}	8.0×10^{-3}	2.9×10^{-2}	9.8×10^{-2}	3.0×10^{-1}
2500	2.5×10^{-3}	9.6×10^{-3}	3.5×10^{-2}	1.2×10^{-1}	3.5×10^{-1}

Comments

Assuming that the step size down is constant at 500 cm^{-1} and 1000 cm^{-1} for N_2 and C_5H_{10} respectively we find for temperatures in excess of 900 K the following relations for Log $k_{c+d}/k_{c+d,\infty}$ and Log $k_c/(k_{c+d})$ at 0.1,1,and 10 atms. repsectively.

Log (k_{c+d}(N2,0.1)/$k_{c+d,\infty}$) =
$-1.9084+5.4890\times10^{-3}T-4.5978\times10^{-6}T^{2}+9.4969\times10^{-10}T^{3}$

Log (k_{c+d}(N_2,1.0)/$k_{c+d,\infty}$) =
$-1.8581+4.7581\times10^{-3}T-3.5095\times10^{-6}T^{2}+6.3896\times10^{-10}T^{3}$

Log (k_{c+d}(N_2,10)/$k_{c+d,\infty}$) =
$-0.9992+2.3566\times10^{-3}T-1.5300\times10^{-6}T^{2}+2.1045\times10^{-10}T^{3}$

Log (k_{c+d}(C_5H_{10},0.1)/$k_{c+d,\infty}$) =
$-1.9837+5.2893\times10^{-3}T-4.0974\times10^{-6}T^{2}+7.9028\times10^{-10}T^{3}$

Log (k_{c+d}(C_5H_{10},1.0)/$k_{c+d,\infty}$) =
$-1.3106+3.2067\times10^{-3}T-2.2098\times10^{-6}T^{2}+3.5092\times10^{-10}T^{3}$

Log (k_{c+d}(C_5H_{10},10)/$k_{c+d,\infty}$) =
$-0.4987+1.0908\times10^{-3}T-6.0180\times10^{-7}T^{2}+3.4893\times10^{-11}T^{3}$

Log ($k_c/(k_{c+d})$,N_2,0.1) =
$-0.1932+3.3533\times10^{-4}T-4.0335\times10^{-8}T^{2}-9.3757\times10^{-11}T^{3}$

Log ($k_c/(k_{c+d})$,N_2,1) =
$+0.1125-3.3027\times10^{-4}T+3.1937\times10^{-7}T^{2}-1.0478\times10^{-10}T^{3}$

Log ($k_c/(k_{c+d})$,N_2,10) =
$+0.0204-6.0218\times10^{-5}T+5.9055\times10^{-8}T^{2}-1.9854\times10^{-11}T^{3}$

Log ($k_c/(k_{c+d})$,C_5H_{10},0.1) =
$+0.1121-3.6249\times10^{-4}T+3.9015\times10^{-7}T^{2}-1.4280\times10^{-10}T^{3}$

Log ($k_c/(k_{c+d})$,C_5H_{10},1) =
$+0.0523-1.4770\times10^{-4}T+1.3709\times10^{-7}T^{2}-4.3368\times10^{-11}T^{3}$

Log ($k_c/(k_{c+d})$,C_5H_{10},10) =
$+0.0034-1.1759\times10^{-5}T+1.3793\times10^{-8}T^{2}-5.4638\times10^{-12}T^{3}$

References

James, D. G. L. and Troughton, G. E.; "Reactions of Allylic Radicals, Part I: Disproportionation between Allyl and Ethyl Radicals", Trans. Faraday Soc., **62**, 145, 1966.

W. Tsang
September, 1988

47,18 C_3H_5(allyl)+C_2H_4 $\rightleftharpoons$ 4-pentenyl → cyclopentyl → cyclopentene + H

	Conditions		Reaction rate constant	Uncertainty
Reaction/Reference	T range/K	[M] range/cm^3	k/cm^{3}molecule^{-1}s^{-1}	
Sakai *et al.* (1975)	723–763	1×10^{19} ethylene 2.8×10^{17} diallyloxalate pyrolysis is flow system g.c. analysis of products	$1\times10^{-14}\exp(-5776/T)$	
Recommendations			$1\times10^{-14}\exp(-5776/T)$	10

Comments

The main reaction is addition to form 4-pentenyl radical. At combustion temperatures this reaction is reversed. There appears to be a small contribution from a minor channel involving cyclization and hydrogen ejection. Walker and Tsang (unpublished results) have found that the decomposition of 4-pentenyl radical (from 1,7 octadiene decomposition) leads to 2.5 % conversion to cyclopentene. A typical expression for alkyl addition to a 1-olefin is $1\times10^{-13}\exp(-3500/T)$ cm^{3}molecule^{-1}s^{-1} (Kerr and Parsonage, "Evaluated Kinetic Data on Gas Phase Addition Reactions", Butterworths, London, 1972). As expected it leads to rate constants that are much larger than those given above. At 1100 K it is 80 times larger than the cyclopentene producing channel and it not far from the factor of 40 deduced from 4-pentenyl decomposition. The recommended rate expression is included to remind the user of the possibility of cyclization.

References

Sakai, T., Nohara, D., and Kunugi, T. "A Kinetic Study on the Formation of Aromatics During Pyrolysis of Petroleum Hydrocarbons" in "Industrial and Laboratory Pyrolyses" (L. F. Albright, B. L. Crynes, ed.) ACS Symposium Series 32 American Chemical Society, Washington, DC, 1976, pg. 152.

Wing Tsang
November, 1988

47,19 C_3H_5+C_2H_3 → 1,4-C_5H_8 (a)
→ C_5H_6 + 2H (b)
→ C_3H_6 + C_2H_2 (c)
→ C_3H_4 + C_2H_4 (d)

	Conditions		Reaction rate constant	Uncertainty
Reaction/Reference	T range/K	[M] range/cm^3	k/cm^{3}molecule^{-1}s^{-1}	
Recommendations			$k_{a+b}=8\times10^{-11}$	2
			$k_c=8\times10^{-12}$	3
			$k_d=4\times10^{-12}$	3
			Log($ka_{+b}/k_{a+b\infty}$,N_2,1.0) = $-5.5048+1.1143\times10^{-2}T$ $-7.0231\times10^{-6}T^2+1.2985\times10^{-9}T^3$	
			Log (k_b/k_{a+b},N_2,1.0) = -17.9735 $+2.6305\times10^{-2}T-1.6929\times10^{-5}T^2$ $+5.5107\times10^{-9}T^3-7.1958\times10^{-13}T^4$	

Comments

There are no data on the kinetics of these processes. The combination reaction is the predominant process. We estimate the high pressure rate constant at 8×10^{-11} cm^{3}molecule^{-1}s^{-1} with an uncertainty of a factor of 2. Some of the newly formed hot molecule can decompose into a hydrogen atom and a 1,4 pentadienyl-3 radical. We estimate the high pressure rate expression for such a process will be k(1,4 pentadiene → 1,4 pentadienyl-3 + H) = $1\times10^{15}\exp(-42600/T)$ s^{-1}. This can be compared with the reverse of k_a which from the thermodynamics and the combination rate constant lead to the expression $k_{-a} = 2\times10^{16}\exp(-40880/T)$ s^{-1}. We have used RRKM calculations to determine the pressure dependence of the recombination process and possible contributions from the hydrogen ejection channel. The results are given in Tables 1–3. The hydrogen ejection process will lead to the formation of 2-cyclopentenyl radical which under combustion conditions will readily eject another hydrogen atom and form cyclopentadiene. However, from the data in Table 2 it is clear that this cannot be an important channel under conditions where the lifetime of vinyl radicals is sufficiently long.

For the disproportionation reactions we recommend

$k_c = 8\times10^{-12}\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$

and

$k_d = 4\times10^{-12}\ \text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$

with an uncertainty of a factor of 3.

TABLE 1. Log ($k_{a+b}/k_{a+b\infty}$) for combination of allyl and vinyl radicals as a function of temperature and pressure assuming strong collisions

T(K)	500	700	900	1100	1300	1500	1700	1900	2100	2300	2500
Log(density)											
16			-0.02	-0.09	-0.24	-0.45	-0.70	-0.94	-1.11	-1.20	-1.23
16.5			-0.01	-0.04	-0.14	-0.30	-0.50	-0.73	-0.93	-1.08	-1.16
17				-0.02	-0.07	-0.18	-0.34	-0.53	-0.73	-0.90	-1.03
17.5				-0.01	-0.03	-0.10	-0.20	-0.35	-0.52	-0.70	-0.85
18					-0.01	-0.05	-0.11	-0.21	-0.34	-0.49	-0.64
18.5					-0.01	-0.02	-0.05	-0.12	-0.20	-0.32	-0.44
19						-0.01	-0.02	-0.05	-0.11	-0.18	-0.27
19.5							-0.01	-0.02	-0.05	-0.09	-0.15
20								-0.01	-0.02	-0.04	-0.07
20.5									-0.01	-0.01	-0.03
21										-0.01	-0.01

TABLE 2. Branching ratio, Log (k_b/k_{a+b}), as a result of the combination of allyl and vinyl radicals as a function of temperature and pressure assuming strong collisions

T(K)	500	700	900	1100	1300	1500	1700	1900	2100	2300	2500
Log(density)											
16	-5.94	-4.14	-2.97	-2.22	-1.69	-1.25	-0.86	-0.52	-0.28	-0.13	-0.06
16.5	-6.44	-4.60	-3.34	-2.51	-1.93	-1.48	-1.10	-0.75	-0.47	-0.26	-0.13
17	-6.94	-5.08	-3.75	-2.84	-2.21	-1.73	-1.34	-1.00	-0.69	-0.44	-0.26
17.5	-7.44	-5.58	-4.21	-3.22	-2.52	-2.00	-1.59	-1.24	-0.94	-0.68	-0.45
18	-7.94	-6.07	-4.69	-3.65	-2.88	-2.30	-1.86	-1.50	-1.20	-0.93	-0.69
18.5	-8.44	-6.57	-5.18	-4.11	-3.29	-2.66	-2.17	-1.79	-1.47	-1.20	-0.95
19	-8.94	-7.07	-5.67	-4.60	-3.74	-3.06	-2.53	-2.11	-1.76	-1.48	-1.23
19.5	-9.44	-7.57	-6.17	-5.09	-4.22	-3.51	-2.94	-2.48	-2.10	-1.79	-1.53
20	-9.94	-8.07	-6.67	-5.59	-4.71	-3.99	-3.39	-2.90	-2.49	-2.16	-1.87
20.5	-10.44	-8.57	-7.17	-6.09	-5.21	-4.48	-3.87	-3.36	-2.93	-2.57	-2.26
21	-10.99	-9.07	-7.67	-6.59	-5.71	-4.97	-4.36	-3.84	-3.40	-3.03	-2.70

Table 3. Collision efficiency as a function of temperature and step size down for the combination of allyl and vinyl radicals

Step Size (cm^{-1})	150	300	600	1200	2400
Temp. (K)					
500	5.7×10^{-2}	1.5×10^{-1}	3.1×10^{-1}	5.1×10^{-1}	6.9×10^{-1}
700	2.8×10^{-2}	8.2×10^{-2}	2.0×10^{-1}	3.8×10^{-1}	5.8×10^{-1}
900	1.4×10^{-2}	4.6×10^{-2}	1.2×10^{-1}	2.7×10^{-1}	4.7×10^{-1}
1100	7.5×10^{-3}	2.6×10^{-2}	7.6×10^{-2}	1.9×10^{-1}	3.6×10^{-1}
1300	4.0×10^{-3}	1.4×10^{-2}	4.5×10^{-2}	1.2×10^{-1}	2.7×10^{-1}
1500	2.2×10^{-3}	8.0×10^{-3}	2.7×10^{-2}	7.9×10^{-2}	1.9×10^{-1}
1700	1.3×10^{-3}	4.8×10^{-3}	1.7×10^{-2}	5.2×10^{-2}	1.4×10^{-1}
1900	7.9×10^{-4}	3.0×10^{-3}	$1.1\times10-2$	3.5×10^{-2}	9.8×10^{-2}
2100	5.0×10^{-4}	1.9×10^{-3}	6.9×10^{-3}	2.3×10^{-2}	6.8×10^{-2}
2300	3.1×10^{-4}	1.2×10^{-3}	4.4×10^{-3}	1.5×10^{-2}	4.5×10^{-2}
2500	1.9×10^{-4}	7.2×10^{-4}	2.7×10^{-3}	9.2×10^{-3}	2.8×10^{-2}

Comments

Assuming that the step size down is constant at 500 cm^{-1} and 1000 cm^{-1} for N_2 and C_5H_6, respectively, we find for temperatures in excess of 900 K the following relations for the fall off behavior and branching ratio at 0.1, 1, and 10 atms. repsectively.

$$\mathrm{Log}\ (k_a+k_b/k_a+k_{b\infty},N_2,0.1) = -15.9635+3.9164\times10^{-2}T-3.3769\times10^{-5}T^2+1.1941\times10^{-8}T^3-1.5039\times10^{-12}T^4$$

$$\mathrm{Log}\ (ka+k_b/k_a+k_{b\infty},N_2,1.0) = -5.5048+1.1143\times10^{-2}T-7.0231\times10^{-6}T^2+1.2985\times10^{-9}T^3$$

$$\mathrm{Log}\ (k_a+k_b/k_a+k_{b\infty},N_2,10.0) = -3.3421+6.1792\times10^{-3}T-3.4600\times10^{-6}T^2+5.3616\times10^{-10}T^3$$

$$\mathrm{Log}\ (k_a+k_b/k_a+k_{b\infty},C_5H_8,0.1) = -4.8903+1.0421\times10^{-2}T-6.9081\times10^{-6}T^2+1.3287\times10^{-9}T^3$$

$$\mathrm{Log}\ (k_a+k_b/k_a+k_{b\infty},C_5H_8,1.0) = -4.4126+8.4697\times10^{-3}T-5.0075\times10^{-6}T^2+8.5308\times10^{-10}T^3$$

$$\mathrm{Log}\ (k_a+k_b/k_a+k_{b\infty},C_5H_8,10.0) = -1.1642+1.8508\times10^{-3}T-7.4867\times10^{-7}T^2+1.7488\times10^{-11}T^3$$

$$\mathrm{Log}\ (k_b/k_a+k_b,N_2,0.1) = -17.3649+2.8343\times10^{-2}T-2.0061\times10^{-5}T^2+7.0578\times10^{-9}T^3-9.8358\times10^{-13}T^4$$

$$\mathrm{Log}\ (k_b/k_a+k_b,N_2,1.0) = -17.9735+2.6305\times10^{-2}T-1.6929\times10^{-5}T^2+5.5107\times10^{-9}T^3-7.1958\times10^{-13}T^4$$

$$\mathrm{Log}\ (k_b/k_a+k_b,N_2,10.0) = -17.6308+2.1113\times10^{-2}T-1.0462\times10^{-5}T^2+2.4880\times10^{-9}T^3-2.2480\times10^{-13}T^4$$

$$\mathrm{Log}\ (k_b/k_a+k_b,C_5H_8,0.1) = -17.5205+2.7472\times10^{-2}T-1.9062\times10^{-5}T^2+6.6340\times10^{-9}T^3-9.1391\times10^{-13}T^4$$

$$\mathrm{Log}\ (k_b/k_a+k_b,C_5H_8,1.0) = -17.4433+2.3061\times10^{-2}T-1.3266\times10^{-5}T^2+3.8437\times10^{-9}T^3-4.4617\times10^{-13}T^4$$

$$\mathrm{Log}\ (k_b/k_a+k_b,C_5H_8,10.0) = -17.2586+1.8693\times10^{-2}T-8.1271\times10^{-6}T^2+1.5795\times10^{-9}T^3-9.5283\times10^{-14}T^4$$

Wing Tsang
September, 1988

47,20 C_3H_5**(allyl)**$+C_2H_2 \rightarrow C_5H_7$ **(a)**
$\rightarrow$ **cyclopentadiene+H (b)**

	Conditions		Reaction rate constant	Uncertainty
Reference	T range/K	[M] range/cm^3	$k/cm^3molecule^{-1}s^{-1}$	
Nohara and Sakai (1980)	703–783	1×10^{19} N_2 1.6% acetylene 2.6% diallyloxalate atmospheric flow reactor; 2–15 s residence time gc analysis of all products	$k_b=6.6\times10^{-10}\exp(-12536/T)$	
Recommendations	 700–800		$k_a=5.3\times10^{\ 14}\exp(-3500/T)$ $k_b=6.6\times10^{-10}\exp(-12526/T)$ (see comments)	10 3

Comments

We estimate that the rate constant for addition of allyl to acetylene will be similar to that for the addition of alkyl radicals to acetylene. We therefore recommend the expression

$$k(C_3H_5(\mathrm{allyl})+C_2H_2 \rightarrow 1{,}4\ \mathrm{pentadienyl}) = 5.3\times10^{-14}\exp(-3500/T)\ cm^3molecule^{-1}s^{-1}$$

with an uncertainty of a factor of 10 under combustion conditions. The rate expression deterrmined by Nohara and Sakai involves the following reactions

$$C_3H_5 + C_2H_2 \rightleftharpoons 1{,}4\ \mathrm{pentadienyl} \rightleftharpoons \mathrm{cyclopentenyl\text{-}3} \rightleftharpoons \mathrm{cyclopentadiene} + H$$

where the $\rightleftharpoons$ signifies the possibilty of the reaction being reversed and does not describe an elementary reaction. The very high activation energy and A-factor suggests that one of these processes may not be reversed. We suggest the use of the experimental expression with great caution and only near the temperature range actually covered. In other cases the expression for addition, k_a, can be used as an upper limit for cyclopentadiene formation.

References

Nohara, D. and Sakai, T. "Kinetic Study on Cycloaddition of Ally Radical to Acetylene" Ind. Eng. Chem. Fundam. **19**, 4, 1980

W. Tsang
February, 1989

47,21 $C_3H_5(allyl)+C_2H \rightarrow C_5H_6$ (a)
$\rightarrow C_2H_3 + C_3H_3$ (b)
$\rightarrow C_5H_5 + H$ (c)
$\rightarrow C_3H_4 + C_2H_2$ (d)

Reference	Conditions T range/K	[M] range/cm^3	Reaction rate constant k/cm^{3}molecule^{-1}s^{-1}	Uncertainty
Recommendations:			$k_a+k_b+k_c = 8\times10^{-11}$	3
			$k_b/k_c = 20$	3
			$\mathrm{Log}[(k_{b+c})/(k_{a+b+c}),N_2,1.0] = -6.4434+1.0743\times10^{-2}T -5.8204\times10^{-6}T^2+1.0250\times10^{-9}T^3$	
			$k_d/k_{a+b+c} = 0.15$	3

Comments

There have been no studies on the rate constants for these reactions. The main reaction is combination (a), followed by the decomposition or stabilization of hot adducts under appropriate pressure and temperature conditions (b and c). We suggest a combination rate constant of $k_{a+b+c} = 8 \times 10^{-11}$ cm^{3}molecule^{-1}s^{-1} with an uncertainty of a factor of 3. The exothermicity of reactions (b) and (c) are similar. The much larger A-factor for the formation of propargyl and vinyl (b) will make this the preferred channel. We recommend $k_b/k_c=20$ with an uncertainty of a factor of 2. The branching ratio for decomposition versus combination plus decomposition $(k_{b+c})/(k_{a+b+c})$ have been derived on the basis of RRKM calculations. Due to the exothermicity of these processes the overall reaction is independent of pressure.

Details regarding branching ratios and weak collision effects are summarized in Table 1 and 2.

TABLE 1. Branching ratio $\mathrm{Log}(k_{b+c})/(k_{a+b+c})$ from the combination of vinyl and C_2H radicals as a function of temperature and pressure assuming strong collisions

T(K)	500	700	900	1100	1300	1500	1700	1900	2100	2300	2500
Log(density)											
16	−0.39	−0.15	−0.06	−0.02	−0.01						
16.5	−0.70	−0.32	−0.13	−0.05	−0.02	−0.01					
17	−1.10	−0.58	−0.28	−0.13	−0.06	−0.03	−0.01	−0.01			
17.5	−1.55	−0.92	−0.50	−0.25	−0.13	−0.06	−0.03	−0.02	−0.01		
18	−2.03	−1.34	−0.80	−0.46	−0.25	−0.14	−0.07	−0.04	−0.02	−0.01	−0.01
18.5	−2.52	−1.80	−1.19	−0.74	−0.45	−0.27	−0.16	−0.09	−0.05	−0.03	−0.02
19	−3.02	−2.28	−1.63	−1.11	−0.74	−0.48	−0.30	−0.19	−0.12	−0.08	−0.05
19.5	−3.52	−2.78	−2.10	−1.54	−1.11	−0.77	−0.53	−0.36	−0.24	−0.16	−0.11
20	−4.02	−3.28	−2.59	−2.01	−1.53	−1.14	−0.84	−0.61	−0.44	−0.32	−0.23
20.5	−4.52	−3.78	−3.09	−2.50	−2.00	−1.58	−1.24	−0.96	−0.74	−0.56	−0.43
21	−5.02	−4.28	−3.59	−2.99	−2.49	−2.05	−1.68	−1.37	−1.11	−0.90	−0.73

TABLE 2.. Collision efficiency as a function of temperature and step size down for the combination of methyl and ethyl radicals

Step Size	150	300	600	1200	2400
Temp. (K)					
500	6.3×10^{-2}	1.6×10^{-1}	3.3×10^{-1}	5.3×10^{-1}	7.1×10^{-1}
700	3.4×10^{-2}	9.6×10^{-2}	2.2×10^{-1}	4.1×10^{-1}	6.1×10^{-1}
900	1.9×10^{-2}	5.9×10^{-2}	1.5×10^{-1}	3.2×10^{-1}	5.2×10^{-1}
1100	1.2×10^{-3}	3.7×10^{-2}	1.1×10^{-1}	2.4×10^{-1}	4.3×10^{-1}
1300	7.0×10^{-3}	2.4×10^{-2}	7.1×10^{-2}	1.8×10^{-1}	3.5×10^{-1}
1500	4.3×10^{-3}	1.5×10^{-3}	4.8×10^{-2}	1.3×10^{-2}	2.8×10^{-1}
1700	2.7×10^{-3}	9.8×10^{-3}	3.2×10^{-2}	9.3×10^{-2}	2.2×10^{-1}
1900	1.7×10^{-3}	6.4×10^{-3}	2.2×10^{-2}	6.7×10^{-2}	1.7×10^{-1}
2100	1.2×10^{-3}	4.3×10^{-3}	1.5×10^{-2}	4.8×10^{-2}	1.3×10^{-1}
2300	8.0×10^{-4}	3.0×10^{-3}	1.1×10^{-2}	3.6×10^{-2}	1.0×10^{-1}
2500	5.7×10^{-4}	2.2×10^{-3}	7.9×10^{-3}	2.7×10^{-2}	7.8×10^{-2}

Comments

Assuming that the step size down is constant at 500 cm^{-1} and 1000 cm^{-1} for N_2 and C_5H_6, respectively, we find for temperatures in excess of 900 K the following relation for the branching ratio $\text{Log}(k_b+k_c)/(k_a+k_b+k_c)$ at 0.1, 1,and 10 atm. respectively.

$$\text{Log}\,[(k_{b+c})/(k_{a+b+c}),N_2,0.1] = -4.1779+7.6178\times10^{-3}T-4.4197\times10^{-6}T^2+8.2061\times10^{-10}T^3$$

$$\text{Log}\,[(k_{b+c})/(k_{a+b+c}),N_2,1.0] = -6.4434+1.0743\times10^{-2}T-5.8204\times10^{-6}T^2+1.0250\times10^{-9}T^3$$

$$\text{Log}\,[(k_{b+c})/(k_{a+b+c}),N_2,10.0] = -7.8967+1.1349\times10^{-2}T-5.3977\times10^{-6}T^2+8.4890\times10^{-10}T^3$$

$$\text{Log}\,[(k_{b+c})/(k_{a+b+c}),C_5H_6,0.1] = -5.1554+8.9547\times10^{-3}T-5.0114\times10^{-6}T^2+9.0554\times10^{-10}T^3$$

$$\text{Log}\,[(k_{b+c})/(k_{a+b+c}),C_5H_6,1.0] = -7.0040+1.0747\times10^{-2}T-5.4345\times10^{-6}T^2+9.0406\times10^{-10}T^3$$

$$\text{Log}\,[(k_{b+c})/(k_{a+b+c}),C_5H_6,10.0] = -7.9197+9.9162\times10^{-3}T-4.0895\times10^{-6}T^2+5.5453\times10^{-10}T^3$$

As can be seen from Tables 1 and 2 under most high temperature conditions decomposition is the predominant process.

For the disproportionation reaction we assign a value a factor of 3 larger than the measured number for ethyl and allyl. The uncertainty is a factor of 3.

W. Tsang
September, 1989

47,22 C_3H_5(allyl)+$CH_3CO \rightarrow C_3H_5COCH_3$

	Conditions		Reaction rate constant	Uncertainty
Reference	T range/K	[M] range/cm^3	k/cm^{3}molecule^{-1}s^{-1}	
Recommendations			3×10^{-11}	2

Comments

Although there are no data on the kinetics of this reaction, there can be little question that the only reaction will be combination with a rate constant, which can be derived from the geometric mean rule, of 3 × 10^{-11} cm^{3}molecule^{-1}s^{-1} with an uncertainty of a factor of 2.

Wing Tsang
September, 1988

47,23 C_3H_5(allyl)+$CH_3OO \rightarrow C_2H_3CHO + H + CH_3O$

	Conditions		Reaction rate constant	Uncertainty
Reference	T range/K	[M] range/cm^3	k/cm^{3}molecule^{-1}s^{-1}	
Recommendations			1.6×10^{-11}	2.5

Comments

There are no data on the rate constants or mechanisms for this reaction. The main process is almost certainly combination to form the peroxide, which under combustion conditions will decompose to form the the methoxy radical, hydrogen atom and acrolein. We estimate the rate constant to be 1.6×10^{-11} cm^{3}molecule^{-1}s^{-1} with an uncertainty of a factor of 2.5.

Wing Tsang
January, 1990

47,24 $C_3H_5(allyl) + CH_3O \rightarrow C_3H_6 + CH_2O$

Reference	Conditions T range/K	 [M] range/cm^3	Reaction rate constant k/cm^{3}molecule^{-1}s^{-1}	Uncertainty
Recommendations			5×10^{-11}	3

Comments

There are no data on the mechanisms and rates of this reaction. In line with the behavior of alkyl radicals one expects that disproportionation will be an important process. Furthermore the only other reaction with comparable rate constants will be combination to form allylmethylether which will readily decompose under combustion conditions to form the same products. We therefore recommend the rate expression 5×10^{-11} cm^{3}molecule^{-1}s^{-1} with an uncertainty of a factor of 3.

Wing Tsang
August, 1988

47,25 $C_3H_5(allyl) + {}^1CH_2 \rightarrow C_4H_7 \rightarrow 1{,}3C_4H_6 + H$ (a)
$\rightarrow C_2H_4 + C_2H_3$ (b)

Reference	Conditions T range/K	 [M] range/cm^3	Reaction rate constant k/cm^{3}molecule^{-1}s^{-1}	Uncertainty
Recommendations			$k_{a+b}=4\times10^{-10}$	3
			$k_a/k_b=5$	3

Comments

Although there are no measurements on the rate constants for this reaction, practically all the insertion and addition products will lead to the formation of hot butenyl-2 or butenyl-3 radicals which will readily decompose to 1,3-butadiene and a hydrogen atom or vinyl and ethylene. The rate constant will be extremely large and we recommend the value

$$k_{a+b}= 4 \times 10^{-10}\ \text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$$

with an uncertainty of a factor of 3. It is difficult to make an estimate of the relative importance of the two decomposition channels. The excess energy for channel (a) when the butenyl-3 radical is formed is about 30 kJ larger than for channel (b). This is however partly compensated for by a somewhat lower A-factor. Formation of butenyl-2 will lead exclusively to channel (a). Insertion into the C–H bond in the 2 position will lead to an isobutenyl radical which will decompose to form allene and a methyl radical. We expect that this will be only a few percent of the major process.

W. Tsang
September, 1988

47,26 $C_3H_5(allyl) + {}^3CH_2 \rightarrow C_4H_7 \rightarrow C_4H_6 + H$ (a)
$\rightarrow C_2H_3 + C_2H_4$ (b)

Reference	Conditions T range/K	 [M] range/cm^3	Reaction rate constant k/cm^{3}molecule^{-1}s^{-1}	Uncertainty
Recommendations			$k_{a+b}=5\times10^{-11}$	2.5
			$k_a/k_b=4$	3

Comments

There are no data on the mechanisms for triplet methylene reaction with allyl. The predominant reaction can only be combination leading to the formation of the 3-butenyl radical with high degree of internal energy. The main mode of decomposition will involve the ejection of a hydrogen to form 1,3-butadiene. A less important mode is decomposition to form vinyl and ethylene. We estimate a rate constant close to collisional or,

$$k_{a+b}=5\times10^{-11}\ \text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$$

with an uncertainty of a factor of 2.5. For reasons similar to that given in (47,25) the branching ratio for the two channels is estimated as a factor of 4. Note that in this case the excess energy is 37 kJ/mol less but butenyl-2 radicals cannot be formed.

W. Tsang
August, 1988

47,38 C_3H_5(allyl) + $CH_3OH \rightarrow C_3H_6 + CH_2OH$

Conditions			Reaction rate constant	Uncertainty
Reference	T range/K	[M] range/cm^3	k/cm^{3}molecule^{-1}s^{-1}	
Log K_p = $1.168-1.761\times10^3/T-3.464\times10^4/T^2+4.995\times10^6/T^3$				
Recommendations			$2.9\times10^{-21}T^{2.9}\exp(-10294/T)$	10

Comment

There are no data on the rate constants for this reaction. Our recommendation is based on our estimate for the reverse reaction (46,39) and the thermodynamics of the reaction. This leads to the following rate expression

$$2.9\times10^{-21}T^{2.9}\exp(-10294/T)\ \mathrm{cm^3molecule^{-1}s^{-1}}$$

with an uncertainty of a factor of 10.

W. Tsang
August, 1988

47,39 C_3H_5(allyl) + $CH_2OH \rightarrow C_3H_6 + CH_2O$

Conditions			Reaction rate constant	Uncertainty
Reference	T range/K	[M] range/cm^3	k/cm^{3}molecule^{-1}s^{-1}	
Recommendations			3×10^{-11}	2.5

Comments

There are no data for the mechanism and rates of this process. Combination will lead to the formation 3-butene-1-ol which will decompose under combustion conditions to form propene and formaldehyde. The disproportionation reaction will lead to the same products. We therefore recommend the rate constant for this overall process as 3×10^{-11} cm^{3}molecule^{-1}s^{-1} with an uncertainty of a factor of 2.5.

Wing Tsang
August, 1988

47,40 C_3H_5(allyl) + $C_3H_8 \rightarrow C_3H_6$ + n-C_3H_7 (a)
$\rightarrow C_3H_6$ + i-C_3H_7 (b)

Conditions			Reaction rate constant	Uncertainty
Reference	T range/K	[M] range/cm^3	k/cm^{3}molecule^{-1}s^{-1}	
Recommendations			$k_a=3.9\times10^{-22}(T)^{3.3}\exp(-9986/T)$ $k_b=1.3\times10^{-22}(T)^{3.3}\exp(-9144/T)$	5 5

Comments

There are no data on the kinetics of these processes. The rate constants for step (a) must be very close to that for allyl attack on ethane. For abstraction of the secondary hydrogen we estimate a rate expression similar to that for abstraction of the primary hydrogens except for changes in reaction path degeneracy and a lowering of the activation energy by 7 kJ/mol. This leads to the rate expressions;

$$k_a = 3.9\times10^{-22}(T)^{3.3}\exp(-9986/T)\ \mathrm{cm^3molecule^{-1}s^{-1}}$$
$$k_b = 1.3\times10^{-22}(T)^{3.3}\exp(-9144/T)\ \mathrm{cm^3molecule^{-1}s^{-1}}$$

The uncertainties are a factor of 5.

Wing Tsang
September, 1988

47,41 C_3H_5(allyl) + n-C_3H_7 $\rightarrow$ 2-C_3H_6 (a)
$\rightarrow$ C_3H_4 + C_3H_8 (b)
$\rightarrow$ 1-C_6H_{12} (c)

Reference	Conditions		Reaction rate constant	Uncertainty
	T range/K	[M] range/cm^3	k/cm^{3}molecule^{-1}s^{-1}	
Recommendations			$k_a = 2.4 \times 10^{-12}\exp(66/T)$	3
			$k_b = 1.2 \times 10^{-12}\exp(66/T)$	3
			$k_c = 3.4 \times 10^{-11}\exp(66/T)$	2

Comments

There are no data on the rates and mechanisms for the reactions of allyl with n-propyl radical. We have used our recommendations for the rate constants of allyl and n-propyl radical combination and the geometric mean rule to derive the following rate expression;

$k_c = 3.4 \times 10^{-11}\exp(66/T)$ cm^{3}molecule^{-1}s^{-1}

We estimate an uncertainty of a factor of 1.5. A check of this number is derived from the shock tube study on hexene-1 decomposition (W. Tsang, Int'l J. Chem. Kin., **10**, 1119, 1978) where through the equilibrium one obtains 2.2×10^{-11} cm^{3}molecule^{-1}s^{-1} with an uncertainty of a factor of 2. At temperatures in excess of 1200 K it is necessary to take into account fall-off effects and the possibility of the chemically activated decomposition of the hot 1-hexene radical to form to propene radicals. However the lifetime of propyl radical is very short at high temperatures. Therefore in general it is not necessary to consider these processes. For the situation where this is not the case we suggest correcting the present results on the basis of the tables in the data sheet for allyl reaction with ethyl (47,17). Our RRKM calculations show that little error will be introduced in this manner.

For the disproportionation process the only existing data (D. G. L. James and G. E. Troughton, Trans. Faraday Soc., 62, 68 (1961)) for ethyl and allyl leads to disproportionation to combination ratios very similar to that for alkyl radicals (M. J. Gibian and R. C. Corley, Chem. Rev., **73**, 443, 1973). On this basis we estimate k_b/k_c = 0.035 and k_a/k_c = 0.07 with an uncertainty of a factor of 2. This leads to the following rate expressions;

$k_a = 2.4 \times 10^{-12}\exp(66/T)cm_3$molecule^{-1}s^{-1}
$k_b = 1.2 \times 10^{-12}\exp(66/T)cm_3$molecule^{-1}s^{-1}

with a total uncertainty of a factor of 3.

W. Tsang
October, 1988

47,42 C_3H_5(allyl) + i-C_3H_7 $\rightarrow$ 2-C_3H_6 (a)
$\rightarrow$ C_3H_4 + C_3H_8 (b)
$\rightarrow$ 4-methylpentene-1 (c)

Reference	Conditions		Reaction rate constant	Uncertainty
	T range/K	[M] range/cm^3	k/cm^{3}molecule^{-1}s^{-1}	
Recommendations			$k_c = 1.9 \times 10^{-10}(T)^{-0.35}\exp(66/T)$	1.5
			$k_a = 3.8 \times 10^{-11}(T)^{-0.35}\exp(66/T)$	3
			$k_b = 7.6 \times 10^{-12}(T)^{-0.35}\exp(66/T)$	3

Comments

There are no data on the rate constants for these reactions. For the combination process, the geometric mean rule and the rate constants for allyl and isopropyl radical combination leads to the rate expression;

$k_c = 1.9 \times 10^{-10}(T)^{-0.35}\exp(66/T)$ cm^{3}molecule^{-1}s^{-1}

with an uncertainty of a factor of 1.5. At temperatures in excess of 1200 K fall-off effects and the chemically activated decomposition of 4-methylpentene-1 will begin to make contributions. However in view of the thermal instability of isopropyl radical (42,1) combination with allyl at these high temperatures is an unlikely process. To arrive at an estimate of the magnitude of these effects use the tables in the data sheets for ethyl and allyl combination.

For the disproportionation process, on the basis of the data for allyl and ethyl (D. G. L. James and G. E. Troughton, Trans. Faraday Soc., **62**, 68 (1961)) and the values for alkyl radicals (M. J. Gibian and R. C. Corley, Chem. Rev., **73**, 441, 1973), we recommend k_a/k_c = 0.2 and k_b/k_c = 0.04 with uncertainties of a factor of 2. this leads to following rate expressions;

$k_a = 3.8 \times 10^{-11}(T)^{-0.35}\exp(66/T)$ cm$_3$molecule^{-1}s^{-1}
$k_b = 7.6 \times 10^{-12}(T)^{-0.35}\exp(66/T)$ cm$_3$molecule^{-1}s^{-1}

W. Tsang
September, 1988

47,43 C_3H_5(allyl) + i-C_4H_{10} $\rightarrow$ C_3H_6 + i-C_4H_9(a)
$\rightarrow$ C_3H_6 + t-C_4H_9(b)

	Conditions		Reaction rate constant	Uncertainty
Reference	T range/K	[M] range/cm^3	$k/cm^3molecule^{-1}s^{-1}$	
Recommendations			$k_a=5.9\times10^{-22}(T)^{3.3}\exp(-9986/T)$ $k_b=0.7\times10^{-22}(T)^{3.3}\exp(-8640/T)$	5 5

Comments

There are no data for the rate constants for these processes. Nevertheless the abstraction of a primary hydrogen should be the same as that in ethane. We therefore recommend the rate expression given for ethane multiplied by 1.5 to take into account the extra hydrogens. For attack on the tertiary hydrogen we reduce the activation energy from that of attack on a secondary hydrogen by 5 kJ/mol. and take into account that there is only one abstractable hydrogen.

The recommended rate expressions are

$$k_a=5.7\times10^{-22}(T)^{3.3}\exp(-10439/T)\ cm^3molecule^{-1}s^{-1}$$
$$k_b=0.7\times10^{-22}(T)^{3.3}\exp(-8640/T)\ cm^3molecule^{-1}s^{-1}$$

with uncertainties of a factor of 5.

W. Tsang
September, 1988

47,44 C_3H_5(allyl) + t-C_4H_9 $\rightarrow$ C_3H_6 + i-C_4H_8 (a)
$\rightarrow$ C_3H_4 + i-C_4H_{10} (b)
$\rightarrow$ 4,4-dimethylpentene-1 (c)

	Conditions		Reaction rate constant	Uncertainty
Reference	T range/K	[M] range/cm^3	$k/cm^3molecule^{-1}s^{-1}$	
Recommendations:			$k_c=1.2\times10^{-9}T^{-0.75}\exp(66/T)$ $k_b=4.8\times10^{-11}T^{-0.75}\exp(66/T)$ $k_a=0.72\times10^{-9}T^{-0.75}\exp(66/T)$	1.5 3 3

Comments

There are no kinetic data on these reactions. From the geometric mean rule and the recommendations for allyl and t-butyl radical combination we arrive at the following rate expression for the combination of allyl and t-butyl radical,

$$k_c = 1.2\times10^{-9}T^{-0.75}\exp(66/T)cm^3molecule^{-1}s^{-1}$$

with an uncertainty of a factor of 1.5. At temperatures in excess of 1100 K fall-off effects begin to be of some importance. However the relative instability of t-butyl radical is such that the combination reaction can only be of importance at lower temperatures. This is also the case for the chemically activated decomposition of the hot 4-methylpentene-1 immediately after combination. To obtain an upper limit for this process use the tables in data sheet (47,17).

For the disporportionation reactions, assumming that allyl and alkyl radicals behave in similar fashion we estimate $k_b/k_c=0.04$ and $k_a/k_c=0.6$. This leads to the following rate expressions

$$k_b=4.8\times10^{-11}T^{-0.75}\exp(66/T)cm^3molecule^{-1}s^{-1}$$
$$k_a=0.72\times10^{-9}T^{-0.75}\exp(66/T)cm^3molecule^{-1}s^{-1}$$

with an uncertainty of a factor of 3.

W. Tsang
September, 1988

47,45 C_3H_5(allyl) + i-C_4H_9 → C_3H_6 + i-C_4H_8 (a)
→ C_3H_4 + i-C_4H_{10} (b)
→ 5-methylhexene-1 (c)

Reference	Conditions T range/K	 [M] range/cm^3	Reaction rate constant k/cm^{3}molecule^{-1}s^{-1}	Uncertainty
Recommedations:			$k_c = 3.4 \times 10^{-11}\exp(66/T)$	1.5
			$k_b = 1.3 \times 10^{-12}\exp(66/T)$	3
			$k_a = 1.3 \times 10^{-12}\exp(66/T)$	3

Comments

There are no data. Our recommendation is based on the combination rates for allyl(47,47) and isobutyl(44,44) radicals and the geometric mean rule. This leads to the rate expression

$$k_c = 3.4 \times 10^{-11}\exp(66/T) \text{ cm}^3\text{molecule}^{-1}\text{s}^{-1}$$

with an uncertainty of a factor of 1.5. At temperatures in excess of 1200 K fall-off effects will slow the rate constants for combination. However in view of the instability of isobutyl radical, one expects that its concentration will be too low to make significant contributions at the higher temperatures. Thus the recommended high pressure rate expression should be used in all cases. This is also the case for the chemically activated decomposition of the hot 5-methylhexene-1 to form isobutene and propylene. If necessary the tables in the data sheet for ethyl and allyl, (47,17) should be used to establish an upper limit for energy exchange effects.

For the disproportionation reaction, on the basis of the data for allyl and ethyl, we estimate $k_a/k_c = k_b/k_c = 0.04$. This leads to the rate expressions;

$$k_a = k_b = 1.3 \times 10^{-12}\exp(66/T) \text{ cm}^3\text{molecule}^{-1}\text{s}^{-1}$$

with an uncertainty of a factor of 3.

W. Tsang
September, 1988

47,46 C_3H_5(allyl) + C_3H_6 → methylcylopentanyl → methylcyclopentene + H

Reference	Conditions T range/K	 [M] range/cm^3	Reaction rate constant k/cm^{3}molecule^{-1}s^{-1}	Uncertainty
Recommendations			$1 \times 10^{-14}\exp(-5776/T)$	10

Comments

There are no data on the kinetics of this reaction. It should however, follow closely the general pattern for the allyl + ethylene reaction (47,18). The initial process will be terminal addition at the double bond. At combustion temperatures this will usually be reversed. A small alternative channel will lead to the formation of methyl cyclopentene and we suggest the use of the expression recommended for the allyl + ethylene reaction with an uncertainty of a factor of 10.

Wing Tsang
September, 1988

47,47 C_3H_5(allyl) + C_3H_5(allyl) → C_6H_{10} (1,5 hexadiene) (a)
→ C_3H_4 + C_3H_6 (b)

	Conditions		Reaction rate constant	Uncertainty
Reference	T range/K	[M] range/cm^3	k/cm^{3}molecule^{-1}s^{-1}	
Tulloch *et al.* (1982)	293–579	$7-350\times10^{14}$ hexadiene in $0-10^{19}$ argon 193 nm laser flash photolysis; spectroscopic detection of allyl	$k_a=1.7\times10^{-11}\exp(132/T)$	2
Rossi *et al.* (1978)	625–900	very low pressure pyrolysis of diallyl oxalate and 3,3′-azo-1-propene. MS detection.	$k_a(625)=1.1\times10^{-11}$ $\infty,p\ =2.9\times10^{-11}$ $k_a(900)=3.2\times10^{-12}$ $\infty,p\ =7\times10^{-11}$	3
van den Bergh and Callear (1970)	300	flash photolysis of 1,5 hexadiene in 1×10^{18} N_2	$k_a=1.4\times10^{-11}$	2
James and Kambanis (1969)	403–463	decomposition of 2×10^{17} diallyl oxalate	$k_b/k_a=0.008$	1.2
Golden *et al.* (1969)	913, 1063	very low pressure pyrolysis of diallyl oxalate. MS detection	$k(913)=1.2\times10^{-11}$ $k(1063)=\ 0.8\times10^{-11}$	3
Recommendations			$k_{a\infty}=1.7\times10^{-11}\exp(132/T)$ $\log\,[k_a/k_{a\infty},N_2,0.1)=$ $-1.309+3.052\times10^{-3}T-2.075\times10^{-6}T^2$ $+3.347\times10^{-10}T^3$	2
			$k_b=1.4\times10^{-13}\exp(132/T)$	2.5

Comments

The accuracy of the spectroscopic studies are dependent upon the absorption coefficient of the allyl radical. Our recommendation is based on the results of Tulloch *et al.* and the uncertainy is the difference between their results and that of van den Bergh and Callear. The directly measured numbers from the low pressure pyrolysis studies have to be corrected for fall-off effects. A summary of the existing data and our recommendations can be found in Fig. 1.

At higher temperatures the combination of allyl radicals are slowed by fall-off effects the results of our RRKM calculations can be found in Tables 1 and 2.

For N_2 or a C_6 hydrocarbon such as hexadiene as the third body we recommend at 0.1, 1 and 10 atm the following k/k_∞ expressions for allyl radical self combination. These expressions are based on a step size down of 500 cm^{-1} for N_2 and 1000 cm^{-1} for 1,5 hexadiene. The applicable temperature range is above 900 K;

$$\text{Log}\,[k_a/k_{a\infty},N_2,0.1)=$$
$$-1.310+3.739\times10^{-3}T-3.020\times10^{-6}T^2+5.474\times10^{-10}T^3$$

$$\text{Log}\,[k_a/k_{a\infty},N_2,1.0)=$$
$$-1.309+3.052\times10^{-3}T-2.075\times10^{-6}T^2+3.347\times10^{-10}T^3$$

$$\text{Log}\,[k_a/k_{a\infty},N_2,10)=$$
$$-0.583+1.207\times10^{-3}T-6.964\times10^{-7}T^2+7.805\times10^{-11}T^3$$

$$\text{Log}\,[k_a/k_{a\infty},C_6H_{10},0.1)=$$
$$-1.361+3.419\times10^{-3}T-2.493\times10^{-6}T^2+4.224\times10^{-10}T^3$$

$$\text{Log}\,[k_a/k_{a\infty},C_6H_{10},1.0)=$$
$$-0.889+1.942\times10^{-3}T-1.216\times10^{-6}T^2+1.686\times10^{-10}T^3$$

$$\text{Log}\,[k_a/k_{a\infty},C_6H_{10},10)=$$
$$-0.203+3.693\times10^{-4}T-1.538\times10^{-7}T^2-1.035\times10^{-11}T^3$$

The uncertainties should not exceed a factor of 2

TABLE 1. Log (k/k_∞) for the combination of allyl radicals as a function of temperature and pressure assuming strong collisions

T(K)	900	1100	1300	1500	1700	1900	2100	2300	2500
Log(density)									
16	−0.04	−0.14	−0.34	−0.63	−0.97	−1.34	−1.71	−2.06	−2.39
16.5	−0.01	−0.07	−0.20	−0.41	−0.68	−0.99	−1.31	−1.63	−1.94
17	−0.01	−0.03	−0.11	−0.25	−0.45	−0.69	−0.96	−1.23	−1.50
17.5		−0.01	−0.05	−0.13	−0.27	−0.44	−0.65	−0.88	−1.11
18			−0.02	−0.06	−0.14	−0.26	−0.41	−0.58	−0.76
18.5			−0.01	−0.03	−0.07	−0.13	−0.22	−0.34	−0.47
19				−0.01	−0.03	−0.06	−0.11	−0.18	−0.26
19.5					−0.01	−0.02	−0.04	−0.08	−0.12
20						−0.01	−0.02	−0.03	−0.05
20.5							−0.01	−0.01	−0.02
21									−0.01

TABLE 2: Collision efficiency as a function of temperature and step size down for allyl radical combination

	150	300	600	1200	2400
Temp(K)					
900	8.2×10^{-3}	2.7×10^{-2}	8.1×10^{-2}	2.0×10^{-1}	3.8×10^{-1}
1100	3.7×10^{-3}	1.3×10^{-2}	4.2×10^{-2}	1.2×10^{-1}	2.6×10^{-1}
1300	2.2×10^{-3}	8.2×10^{-3}	2.8×10^{-2}	8.5×10^{-2}	2.2×10^{-1}
1500	1.9×10^{-3}	7.2×10^{-3}	2.5×10^{-2}	8.2×10^{-2}	2.3×10^{-1}
1700	2.1×10^{-3}	8.0×10^{-3}	2.9×10^{-2}	9.5×10^{-2}	2.8×10^{-1}
1900	2.6×10^{-3}	9.9×10^{-3}	3.6×10-2	1.2×10^{-1}	3.5×10^{-1}
2100	3.3×10^{-3}	1.2×10^{-2}	4.4×10^{-2}	1.5×10^{-1}	4.3×10^{-1}
2300	4.0×10^{-3}	1.5×10^{-2}	5.4×10^{-2}	1.8×10^{-1}	5.2×10^{-1}
2500	4.8×10^{-3}	1.8×10^{-2}	6.3×10^{-2}	2.1×10^{-1}	5.9×10^{-1}

We accept the results of James and Kambanis on the disproportionation to combination rate constant ratio. This leads to

$$k_b = 1.4\times10^{-13}\exp(132/T)\ \mathrm{cm^3 molecule^{-1} s^{-1}}$$

with an uncertainty of a factor of 2.5.

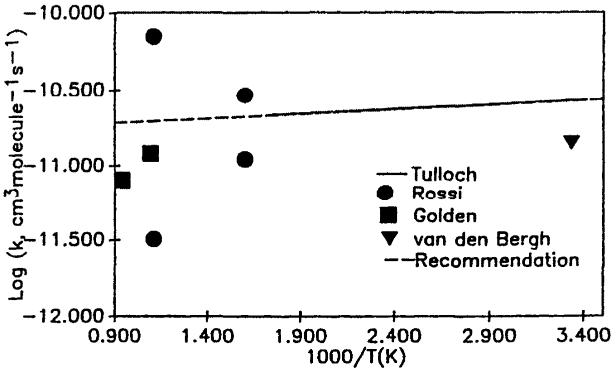

FIG. 1. Summary of Experimental Data and Recommendation on Allyl Radical Combination. The two values of Rossi *et al.* (filled circles at the same temperature) are the experimental numbers and corrected values after taking into account fall-off. The work of Golden *et al.* are the directly measured numbers. The recommendations are for the high pressure limit.

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van den Bergh, H. E. and Callear, A. B., "Experimental Determination of the Oscillator Strength of the $B(^2B_1)-X(^2A_2)$ Transition of the Free Alkyl Radical" , Trans. Faraday Society., **66**, 2681, 1970.

Wing Tsang
September, 1988

4. Thermodynamic Data Tables

46 C_3H_6

	J mol^{-1} K^{-1}		kJ·mol^{-1}	
T/K	C_p	S	ΔH_f	ΔG_f
300	64.18	267.36	20.33	62.97
500	107.53	307.40	11.69	93.93
700	118.70	343.26	5.44	127.99
900	136.82	375.39	1.42	163.59
1100	150.58	404.22	−0.75	199.91
1300	161.04	430.28	−1.76	236.48
1500	168.62	453.88	−2.01	273.13

$\text{Log}_{10}K_p = 9.82894 + 738.643/T - 426407/T^2 + 3.07673\times10^7/T^3$

Rossini, F. D., Pitzer, K. S., Arnett, R. L., Braun, R. M., and Pimentel, G. C., "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds" Carnegie Press, Carnegie Institute of Technology, Pittsburgh, Pa., 1953.

47 C_3H_5**(allyl)**

	J·mol^{-1} K^{-1}		kJ·mol^{-1}	
T/K	C_p	S	ΔH_f	ΔG_f
300	60.89	260.14	169.03	194.24
500	89.82	298.25	162.53	212.95
700	111.04	332.06	158.02	233.98
900	126.39	361.90	155.13	256.09
1100	137.92	388.44	153.63	278.70
1300	146.67	412.22	153.02	301.47
1500	153.36	433.70	152.91	324.33

$\text{Log}_{10}K_p = -6.1453–7.540\times10^3/T - 2.9431\times10^5/T^2 + 1.9825\times10^7/T^3$

Frequencies (degeneracy) 400 (2), 500(1), 950(2), 1100(3), 1300(3), 1430(2), 3050(2), 3100(3); Product of Moments of Inertia 1.5×10^{-115} gm^3·cm^6, Symmetry number = 2; Ground State Degeneracy = 2.

5. Transport Properties (Lennard-Jones Potential) for Unimolecular Reactions

Substance	σ/Å	(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(H_2)	2.827	59.7
Nitrogen(N_2)	3.798	71.1
Oxygen(O_2)	3.467	106.7
Sulfur Hexafluoride	5.128	222.1
Water	2.641	804.1
Methanol	3.626	481.8
Hydroxymethyl	same values as for methanol	
Propane	5.118	237.1
n-Propyl	same values as for propane	
i-Propyl	" " " " "	
Isobutane	5.278	330.1
t-Butyl	same values as for isobutane	
i-Butyl	" " " " "	
Propene	4.678	298.9
Allyl	same values as for propene	

From Reid, R. C., Prausnitz, J. M. and Poling, B. E., "The Properties of Gases and Liquids" McGraw-Hill Book Company, New York, 1987.