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Chemical Kinetic Data Base for Combustion Chemistry Part 4. Isobutane

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Chemical Kinetic Data Base for Combustion Chemistry Part 4. Isobutane

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This publication contains evaluated and estimated data on the kinetics of reactions involving isobutane, *t*-butyl radical and isobutyl radical and various small inorganic and organic species which are of importance for the proper understanding of 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 and propane pyrolysis and combustion, but which also contains a large volume of data that are applicable to the isobutane 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: *t*-butyl radical, combustion, database, gas kinetics, isobutyl radical, rate expressions.

Contents

1. Introduction

1.1. Scope

This is the fourth of a series of papers[1,2,3] containing evaluated kinetic data on the gas phase reactions of organic fuels. Previously, our publications have covered the methane, ethane, methanol and propane systems. We now expand our coverage to include the reactions involved in the early stages of isobutane combustion and pyrolysis. The new species that are considered are isobutane, *t*-butyl radical and isobutyl radical. As in our earlier work we cover all the reactions of these species with the 30 other compounds that has previously been considered as well as the reactions with itself. Recommendations on the rate expressions for 80 reactions are presented.

The C_4 hydrocarbons considered in this study represent our continuing expansion into larger and more general hydrocarbon fuels. A number of new elements are introduced into the database. These include the presence of the tertiary C—H bond and the corresponding tertiary radical. For the primary radical (isobutyl), there is the possibility of beta C—C bond cleavage. These data represent building blocks for future work dealing with the oxidative and pyrolytic degradation of increasingly more complex and realistic fuels. With the inclusion of isobutane into the database all of the important groupings in the decomposition of simple aliphatic compounds have now been covered. Thus it should now be possible to simulate the initial stages of the pyrolysis and oxidation of most aliphatic hydrocarbons or mixtures thereof. 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 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 was given. Where information on a particular reaction is missing, the implication is that for all possible situations the rate con

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stant is sufficiently small so that it can be safely ignored. The reaction 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, methanol and propane combustion[1,2,3]. It is expected that the data presented here will be used in conjunction with those in the previous publications. In the following, we provide direction neccesary for the use of the information.

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

1.3. Guide to Summary Table

The summary table 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 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

This section 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, methanol and propane combustion system and to the twenty-five species that are labelled from 2 to 26 for the methane system 38–39 for the methanol system and 40–42 or the propane system we now add 43–45 for isobutane, t-butyl and isobutyl, respectively. Since pairs of these numbers form a particular reaction, we now consider reactions of these three compounds with all lower numbered species and with themselves. These sequence numbers are at the top

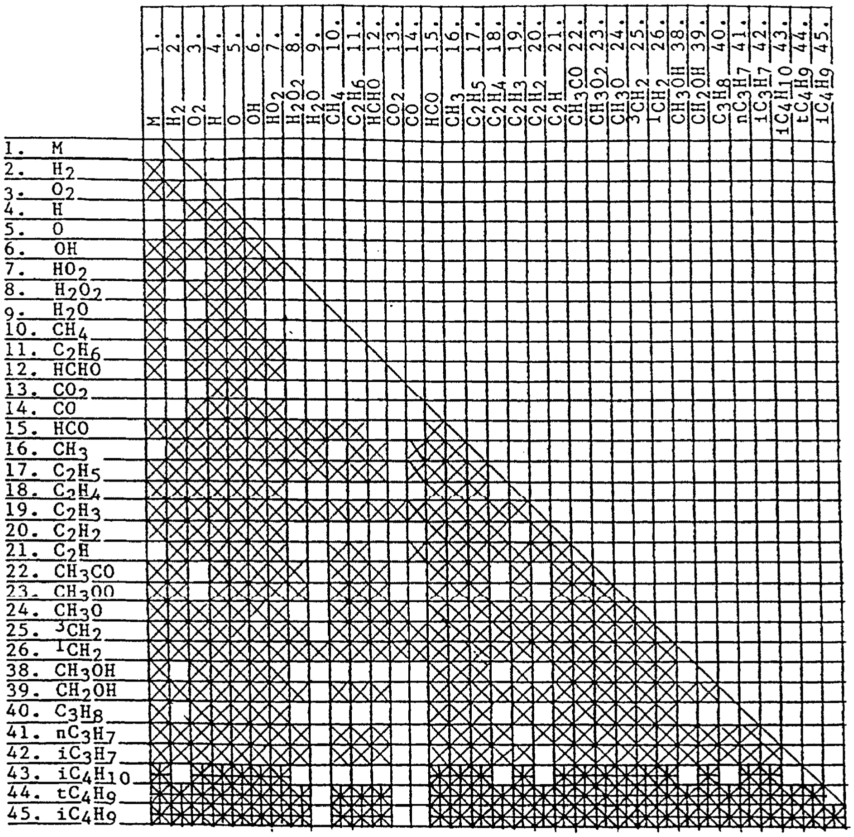

FIG. 1.: Reaction grid: X: Reactions covered in references 1, 2 and 3.
*: Reactions evaluated in current study

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 bimolecular 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[4] transition states to fit hydrogen abstraction data over the 300–2500 K temperature range of interest. This leads in general to a T^2 - T^4 temperature dependence for the 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[5] 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, β (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, β (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, $\beta\ (t)= \beta\ (e) \times \beta\ (c)$,. β (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 isobutane decomposition in the case of a dilute isobutane in argon mixture at 1500 K. We begin by determining β (c). It involves the calculation of a number of ratios. In the following, the numerator refers to the properties of the isobutane-argon mixture, while the denominator refers to pure isobutane 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 isobutane and argon this number is

23.69(isobutane-argon)/29.06(isobutane-isobutane) = .815

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

$$[5.278(\text{isobutane}) + 3.542(\text{argon})] \div [5.278(\text{isobutane})\times 2] = .836$$

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

$$= 1/\{.697 + .5185 \times \log[kT/\epsilon(\text{gas}_1\text{-gas}_2)]\}$$

and

$$\epsilon/k \text{ (argon–isobutane)} = \{[\epsilon(\text{argon–argon})/k][\epsilon(\text{isobutane–isobutane})/k]\}^{5}$$

where ϵ/k is the Lennard Jones well depth. Since ϵ/k is 330.1 for isobutane and 93.3 K for argon, then the ratio of the collision integrals is .847/.963 = .879. The correction factor is then,

$$\beta(c) = C^2W/R^{5} = .68$$

For the isobutane-argon mixture with a 600 cm^{-1} step size down the collision efficiency on a per collision basis at 1500 K is, $\beta(e) = .0272$ (see 43,1). The total collision efficiency is then

$$\beta(t) = \beta(c) \times \beta(e) = .0272 \times .68 = .0185$$

At 2 atmospheres or 10^{19} molecules/cm^3 this is equivalent to a density of 1.85×10^{17} molecules cm^{-3} for isobutane as a strong collider. From Table A of 43,1 we then find $k/k_\infty = 0.45$.

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 an untested approximation. Fortunately, for the systems considered here pressure effects turned out to be relatively unimportant.

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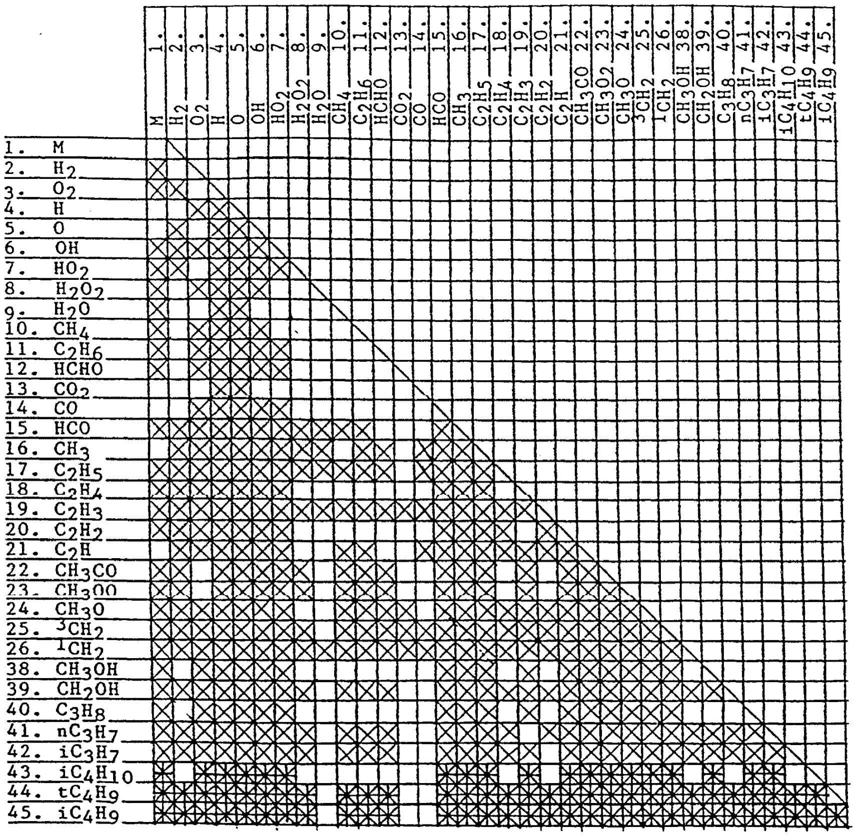

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In the course of carrying out the earlier evaluations[1-3], we found that the data for unimolecular fall-off can generally be fitted in the context of weak collisions by step sizes of 50–100 cm^{-1} near room temperature and 500–800 cm^{-1} under higher temperature combustion conditions (>900 K). This is also borne out in this study for propane decomposition with argon as the weak collider. 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 .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

This section contains thermodynamic and transport properties of isobutane, and *t*-butyl and isobutyl radicals. 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. It should be noted that for the *t*-butyl and isobutyl radicals in our database we use higher values for the heat of formation than those which have been used in the past. We have given detailed justifications for these numbers in an earlier paper.[8] For the present we note that if the more familiar lower values[9] are to be used in the present context, it would have been necessary to reject one or the other set of existing data on either *t*-butyl radical decomposition or hydrogen addition to isobutene. Our examination of the experimental results on these reactions show no reason to reject any of these results. Indeed, they show a remarkable degree of internal consistency. Thus, in order to satisfy detail balance, the higher values of the heat of formation were chosen. In the case of isobutyl radicals we have assumed that the primary C—H bond dissociation energy is equal to that of the primary C—H bond in propane. 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. Acknowledgment

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

1.7. References to the Introduction

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2. Index of Reactions and Summary of Recommended Rate Expressions

No.	Reaction	Rate Constant $k/cm^3\ molecule^{-1}s^{-1}$	Uncertainty factor	Page
43,1	$i\text{-}C_4H_{10} \rightarrow i\text{-}C_3H_7 + CH_3$	$k_\infty=1.1x10^{26}T^{-2.61}exp(-45462/T)s^{-1}$	2	11
		$logk/k_\infty(N_2,1)=-2.047+5.196x10^{-3}T-3.765x10^{-6}T^2+6.442x10^{-10}T^3$		11
43,3	$i\text{-}C_4H_{10} + O_2 \rightarrow HO_2 + i\text{-}C_4H_9$ (a)	$k_a=6.7x10^{-11}exp(-25630/T)$	10	14
	$\rightarrow HO_2 + t\text{-}C_4H_9$ (b)	$k_b=6.6x10^{-11}exp(-22140/T)$	3	14
43,4	$i\text{-}C_4H_{10} + H \rightarrow i\text{-}C_4H_9 + H_2$ (a)	$k_a=3.0x10^{-18}T^{2.54}exp(-3400/T)$	3	14
	$\rightarrow t\text{-}C_4H_9 + H_2$ (b)	$k_b=1.0x10^{-18}T^{2.4}exp(-1300/T)$	3	14
43,5	$i\text{-}C_4H_{10} + O \rightarrow i\text{-}C_4H_9 + OH$ (a)	$k_a=7.1x10^{-19}T^{2.5}exp(-1834/T)$	2	15
	$\rightarrow t\text{-}C_4H_9 + OH$ (b)	$k_b=2.6x10^{-19}T^{2.5}exp(-560/T)$	2	15
43,6	$i\text{-}C_4H_{10} + OH \rightarrow i\text{-}C_4H_9 + H_2O$ (a)	$k_a=3.81x10^{-14}T^{1.53}exp(-390/T)$	1.2	16
	$\rightarrow t\text{-}C_4H_9 + H_2O$ (b)	$k_b=9.52x10^{-14}T^{0.51}exp(-32/T)$	1.2	16
43,7	$i\text{-}C_4H_{10} + HO_2 \rightarrow i\text{-}C_4H_9 + H_2O_2$ (a)	$k_a=5x10^{-20}T^{2.55}exp(-7800/T)$	2 at 750K, 10 at 300K and 2500K	17
	$\rightarrow t\text{-}C_4H_9 + H_2O_2$ (b)	$k_b=6x10^{-21}T^{2.55}exp(-5300/T)$		17
43,15	$i\text{-}C_4H_{10} + HCO \rightarrow i\text{-}C_4H_9 + H_2CO$ (a)	$k_a=5.1x10^{-19}T^{2.5}exp(-9275/T)$	5	18
	$\rightarrow t\text{-}C_4H_9 + H_2CO$ (b)	$k_b=5.7x10^{-20}T^{2.5}exp(-6800/T)$	5	18
43,16	$i\text{-}C_4H_{10} + CH_3 \rightarrow i\text{-}C_4H_9 + CH_4$ (a)	$k_a=2.25x10^{-24}T^{3.65}exp(-3600/T)$	2	18
	$\rightarrow t\text{-}C_4H_9 + CH_4$ (b)	$k_b=1.5x10^{-24}T^{3.46}exp(-2314/T)$	2	18
43,17	$i\text{-}C_4H_{10} + C_2H_5 \rightarrow C_2H_6 + i\text{-}C_4H_9$ (a)	$k_a=2.3x10^{-24}T^{3.65}exp(-4600/T)$	2.5	20
	$\rightarrow C_2H_6 + t\text{-}C_4H_9$ (b)	$k_b=0.9x10^{-24}T^{3.46}exp(-3000/T)$	2.5	20
43,19	$i\text{-}C_4H_{10} + C_2H_3 \rightarrow C_2H_4 + i\text{-}C_4H_9$ (a)	$k_a=2.25x10^{-24}T^{3.65}exp(-2600/T)$	5	20
	$\rightarrow C_2H_4 + t\text{-}C_4H_9$ (b)	$k_b=1.5x10^{-24}T^{3.46}exp(-1314/T)$	5	20
43,21	$i\text{-}C_4H_{10} + C_2H \rightarrow i\text{-}C_4H_9 + C_2H_2$ (a)	$k_a=1x10^{-11}$	3	21
	$\rightarrow t\text{-}C_4H_9 + C_2H_2$ (b)	$k_b=1.1x10^{-12}$	3	21
43,22	$i\text{-}C_4H_{10} + CH_3CO \rightarrow i\text{-}C_4H_9 + CH_3CHO$ (a)	$k_a=5.1x10^{-19}T^{5.1}exp(-9275/T)$	10	21
	$\rightarrow t\text{-}C_4H_9 + CH_3CHO$ (b)	$k_b=5.7x10^{-20}T^{2.5}exp(-6800/T)$	10	21
43,23	$i\text{-}C_4H_{10} + CH_3O_2 \rightarrow i\text{-}C_4H_9 + CH_3O_2H$ (a)	$k_a=5x10^{-20}T^{2.55}exp(-7800/T)$	2 at 750K, 10 at 300K and 2500K	22
	$\rightarrow t\text{-}C_4H_9 + CH_3O_2H$ (b)	$k_b=6x10^{-21}T^{2.55}exp(-5300/T)$	2 at 750K, 10 at 300K and 2500K	22

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

No.	Reaction	Rate Constant $k/cm^3\ molecule^{-1}s^{-1}$	Uncertainty factor	Page
43,24	$i\text{-}C_4H_{10} + CH_3O \rightarrow i\text{-}C_4H_9 + CH_3OH$ (a)	$k_a=0.8\times10^{-12}\exp(-3676/T)$	5 at 400-600K	22
	$\rightarrow t\text{-}C_4H_9 + CH_3OH$ (b)	$k_b=3.8\times10^{-14}\exp(-1446/T)$	10 at 300 and	
			1500K	22
43,25	$i\text{-}C_4H_{10} + {}^3CH_2 \rightarrow CH_3 + i\text{-}C_4H_9$ (a)	$k_a=1.61\times10^{-11}\exp(-3970/T)$	1.3	23
	$\rightarrow CH_3 + t\text{-}C_4H_9$ (b)	$k_b=1.81\times10^{-11}\exp-2467/T)$	300 to 700K	23
	$\rightarrow {}^3CH_2 + i\text{-}C_4H_{10}$ (c)	$k_c=3.7\times10^{-11}\exp(-4481/T)$	5 at 2500K	23
43,26	$i\text{-}C_4H_{10} + {}^1CH_2 \rightarrow C_2H_5 + i\text{-}C_3H_7$ (a)	$k_{a+c}{}^{\infty}=2.3\times10^{-10}$	3	24
	$\rightarrow CH_3 + t\text{-}C_4H_9$ (b)	$\log k_a/k_{a+c}(N_2,1,0)=-11.904+$		
	$\rightarrow$ isopentane (c)	$1.9313\times10^{-2}T-1.082\times10^{-5}T^2+$		
	$\rightarrow$ neopentane (d)	$2.461\times10^{-9}T^3-1.724\times10^{-13}T^4$		24
	$\rightarrow {}^3CH_2 + i\text{-}C_4H_{10}$ (e)	$k_{b+d}=4.0\times10^{-11}$	1.3	24
		$k_e=9.0\times10^{-11}$		24
43,39	$i\text{-}C_4H_{10} + CH_2OH \rightarrow i\text{-}C_4H_9 + CH_3OH$ (a)	$k_a=5.0\times10^{-22}T^{2.95}\exp(-7033/T)$	5	26
	$\rightarrow t\text{-}C_4H_9 + CH_3OH$ (b)	$k_b=2.0\times10^{-22}T^{2.76}\exp(-5433/T)$	5	26
43,41	$i\text{-}C_4H_{10} + n\text{-}C_3H_7 \rightarrow i\text{-}C_4H_9 + C_3H_8$ (a)	$k_a=2.3\times10^{-24}T^{3.65}\exp(-4600/T)$	3	27
	$\rightarrow t\text{-}C_4H_9 + C_3H_8$ (b)	$k_b=0.9\times10^{-24}T^{3.46}\exp(-3000/T)$	3	27
43,42	$i\text{-}C_4H_{10} + i\text{-}C_3H_7 \rightarrow i\text{-}C_4H_9 + C_3H_8$ (a)	$k_a=2.1\times10^{-26}T^{4.2}\exp(-4386/T)$	3	27
	$\rightarrow t\text{-}C_4H_9 + C_3H_8$ (b)	$k_b=2.5\times10^{-27}T^{4.2}\exp(-3000/T)$	5	27
44,1	$t\text{-}C_4H_9 \rightarrow i\text{-}C_4H_8 + H$ (a)	$k_a=8.3\times10^{13}\exp(-19200/T)s^{-1}$	3	28
	$\rightarrow C_3H_6 + CH_3$ (b)	$\log k/k_{\infty}(N_2,1)=-0.305+1.595\times10^{-3}T-$		
		$2.045\times10^{-6}T^2+4.169\times10^{-10}T^3$		28
44,2	$t\text{-}C_4H_9 + H_2 \rightarrow i\text{-}C_4H_{10} + H$	$3.07\times10^{-26}T^{4.24}\exp(-4510/T)$	3	30
44,3	$t\text{-}C_4H_9 + O_2 \rightarrow i\text{-}C_4H_8 + HO_2$	8×10^{-13}	3	31
44,4	$t\text{-}C_4H_9 + H \rightarrow i\text{-}C_4H_8 + H_2$ (a)	$k_a=9\times10^{-12}$	2	31
	$\rightarrow i\text{-}C_4H_{10}$ (b)	$k_{b+c}=4\times10^{-11}$	2	31
	$\rightarrow i\text{-}C_3H_7 + CH_3$ (c)	$\log k_c/k_{b+c}=-10.882+1.893\times10^{-2}T-$		
		$1.191\times10^{-5}T^2+3.183\times10^{-9}T^3-2.999\times10^{-13}T^4$		31
44,5	$t\text{-}C_4H_9 + O \rightarrow i\text{-}C_4H_8 + OH$ (a)	$k_a=3\times10^{-10}$	3	33
	$\rightarrow CH_3COCH_3 + CH_3$ (b)	$k_a/k_b=1$	4	33
44,6	$t\text{-}C_4H_9 + OH \rightarrow i\text{-}C_4H_8 + H_2O$	3×10^{-11}	3	34
44,7	$t\text{-}C_4H_9 + HO_2 \rightarrow CH_3 + CH_3COCH_3 + OH$	3×10^{-11}	2	34
44,8	$t\text{-}C_4H_9 + H_2O_2 \rightarrow HO_2 + C_4H_{10}$	$4.2\times10^{-26}T^{3.79}\exp(-136/T)$	5	34
44,10	$t\text{-}C_4H_9 + CH_4 \rightarrow i\text{-}C_4H_{10} + CH_3$	$8.2\times10^{-31}T^{5.38}\exp(-5996/T)$	3	35

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

No.	Reaction	Rate Constant k/cm^3 molecule$^{-1}s^{-1}$	Uncertainty factor	Page
44,11	$t\text{-}C_4H_9 + C_2H_6 \rightarrow i\text{-}C_4H_{10} + C_2H_5$	$5.6x10^{-30}T^{5.17}exp(-4563/T)$	3	35
44,12	$t\text{-}C_4H_9 + HCHO \rightarrow i\text{-}C_4H_{10} + HCO$	$5.4x10^{-15}exp(-1788/T)$	5	35
44,15	$t\text{-}C_4H_9 + HCO \rightarrow i\text{-}C_4H_{10} + CO$ (a)	$k_a=1x10^{-10}$	5	36
	$\rightarrow t\text{-}C_4H_9CHO$ (b)	$k_b=2x10^{-11}$	5	36
44,16	$t\text{-}C_4H_9 + CH_3 \rightarrow i\text{-}C_4H_8 + CH_4$ (a)	$k_a=2.1x10^{-11}(300/T)$	2	36
	$\rightarrow neo\text{-}C_5H_{12}$ (b)	$k_b=2.7x10^{-11}(300/T)$	2	36
44,17	$t\text{-}C_4H_9 + C_2H_5 \rightarrow i\text{-}C_4H_{10} + C_2H_4$ (a)	$k_a=0.51x10^{-11}(300/T)^{0.75}$	2	37
	$\rightarrow i\text{-}C_4H_8 + C_2H_6$ (b)	$k_b=0.83x10^{-11}(300/T)^{0.75}$	2	37
	$\rightarrow CH_3C(CH_3)_2CH_2CH_3$ (c)	$k_c=1.6x10^{-11}(300/T)^{0.75}$	2	37
44,18	$t\text{-}C_4H_9 + C_2H_4 \rightarrow (CH_3)_3CCH_2CH_2$ (a)			
	$\rightarrow i\text{-}C_4H_8 + C_2H_5$ (b)			
	$\rightarrow C_5H_{10} + CH_3$ (c)			
		$k_{b+c}=4.8x10^{-15}exp(-3190/T)$	3	37
		$k_b/k_c=0.5exp(1200/T)$	1.5	37
44,19	$t\text{-}C_4H_9 + C_2H_3 \rightarrow i\text{-}C_4H_8 + C_2H_4$ (a)	$k_a=0.51x10^{-11}(300/T)^{0.75}$	3	38
	$\rightarrow i\text{-}C_4H_{10} + C_2H_2$ (b)	$k_b=0.83x10^{-11}(300/T)^{0.75}$	3	38
	$\rightarrow C_6H_{12}$ (c)	$k_{c+d\infty}=1.6x10^{-11}(300/T)^{0.75}$	3	38
	$\rightarrow C_5H_9 + CH_3$ (d)	$logk_d/k_{c+d}(N_2,1)=-10.083+1.745x10^{-2}T-1.060x10^{-5}T^2+2.601x10^{-9}T^3$	5	38
44,20	$t\text{-}C_4H_9 + C_2H_2 \rightarrow (CH_3)_3CCH{=}CH$ (a)			
	$\rightarrow CH_2{=}C(CH_3)CH{=}CH_2 + CH_3$ (b)			
		$k_b=4.6x10^{-14}exp(-3323/T)$	3	40
44,21	$t\text{-}C_4H_9 + C_2H \rightarrow i\text{-}C_4H_8 + C_2H_2$ (a)			
	$\rightarrow C_6H_{10}$ (b)			
	$\rightarrow C_5H_7 + CH_3$ (c)			
		$k_{b+c}=1.6x10^{-11}(300/T)^{0.75}$	3	40
		$k_a=0.51x10^{-11}(300/T)^{0.75}$	3	40
		$logk_c/k_{b+c}(N_2,1) = -6.557+1.386x10^{-2}T-1.082x10^{-5}T^2+3.698x10^{-9}T^3-4.672x10^{-13}T^4$		40
44,22	$t\text{-}C_4H_9 + CH_3CO \rightarrow t\text{-}C_4H_9COCH_3$	$1.8x10^{-11}(300/T)^{0.75}$	2	42
44,23	$t\text{-}C_4H_9 + CH_3O_2 \rightarrow CH_3O + CH_3COCH_3 + CH_3$	$2x10^{-11}$	3	42

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

No.	Reaction	Rate Constant $k/\mathrm{cm^3\ molecule^{-1}s^{-1}}$	Uncertainty factor	Page
44,24	$t\text{-}C_4H_9 + CH_3O \rightarrow i\text{-}C_4H_{10} + CH_2O$ (a)	$k_a=1.6\times10^{-11}$	5	42
	$\rightarrow t\text{-}C_4H_9OCH_3$ (b)	$k_b=1.5\times10^{-11}$	3	42
44,25	$t\text{-}C_4H_9 + {}^1CH_2 \rightarrow i\text{-}C_4H_8 + CH_3$	3×10^{-10}	2	43
44,26	$t\text{-}C_4H_9 + {}^3CH_2 \rightarrow i\text{-}C_4H_8 + CH_3$	$2.7\times10^{-11}(300/T)$	2	43
44,38	$t\text{-}C_4H_9 + CH_3OH \rightarrow i\text{-}C_4H_{10} + CH_2OH$ (a)	$k_a=1.3\times10^{-28}T^{4.7}\exp(-4572\ T)$	10	44
	$\rightarrow t\text{-}C_4H_{10} + CH_3O$ (b)	$k_b=2.5\times10^{-21}T^{1.8}\exp(-4709\ T)$	10	44
44,39	$t\text{-}C_4H_9 + CH_2OH \rightarrow i\text{-}C_4H_{10} + HCHO$ (a)	$k_c=1.6\times10^{-11}(300/T)^{0.75})$	2	44
	$\rightarrow C_4H_8 + CH_3OH$ (b)	$k_a=0.8\times10^{-11}(300/T)^{0.75})$	3	44
	$\rightarrow C_5H_{11}OH$ (c)	$k_b=0.5\times10^{-11}(300/T)^{0.75})$	3	44
44,40	$t\text{-}C_4H_9 + C_3H_8 \rightarrow i\text{-}C_4H_{10} + n\text{-}C_3H_7$ (a)	$k_a=1.9\times10^{-29}T^{5.0}\exp(-4808/T)$	6	45
	$\rightarrow i\text{-}C_4H_{10} + i\text{-}C_3H_7$ (b)	$k_b=1.8\times10^{-30}T^{5.16}\exp(-4091/T)$	6	45
44,41	$t\text{-}C_4H_9 + n\text{-}C_3H_7 \rightarrow i\text{-}C_4H_{10} + C_3H_6$ (a)			
	$\rightarrow i\text{-}C_4H_8 + C_3H_8$ (b)			
	$\rightarrow CH_3C(CH_3)_2CH_2CH_2CH_3$ (c)			
		$k_c=1.6\times10^{-11}(300/T)^{0.75})$	1.5	45
		$k_a=0.5\times10^{-11}(300/T)^{0.75})$	2	45
		$k_b=0.8\times10^{-11}(300/T)^{0.75})$	2	45
44,42	$t\text{-}C_4H_9 + i\text{-}C_3H_7 \rightarrow i\text{-}C_4H_{10} + C_3H_6$ (a)			
	$\rightarrow i\text{-}C_4H_8 + C_3H_8$ (b)			
	$\rightarrow CH_3C(CH_3)_2CH(CH_3)_2$ (c)			
		$k_c=1.3\times10^{-11}(300/T)^{1.1}$	1.5	46
		$k_a=0.9\times10^{-11}(300/T)^{1.1}$	1.7	46
		$k_b=0.9\times10^{-11}(300/T)^{1.1}$	1.7	46
44.43	$t\text{-}C_4H_9 + i\text{-}C_4H_{10} \rightarrow i\text{-}C_4H_{10} + i\text{-}C_4H_9$	$8.4\times10^{-30}T^{5.17}\exp(-4563/T)$	4	46
44,44	$2t\text{-}C_4H_9 \rightarrow C_8H_{18}$ (a)	$k_a=4\times10^{-12}(300/T)^{1.5}$	1.5 at 300K, 2 at 1 47K	47
	$\rightarrow C_4H_8 + C_4H_{10}$ (b)	$k_a/k_b=2.7$	1.1	47
45,1	$i\text{-}C_4H_9 \rightarrow C_3H_6 + CH_3$	$2\times10^{13}\exp(-15075/T)s^{-1}$	4	49
		$\log k/k_\infty(N_2,1.0)=-0.120+$ $1.118\times10^{-3}T-1.776\times10^{-6}T^2+$ $3.911\times10^{-10}T^3$		49
45,2	$i\text{-}C_4H_9 + H_2 \rightarrow i\text{-}C_4H_{10} + H$	$4.7\times10^{-21}T^{2.72}\exp(-4930/T)$	3	51

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

No.	Reaction	Rate Constant k/cm^3 $molecule^{-1}s^{-1}$		Uncertainty factor	Page
45,3	$i\text{-}C_4H_9 + O_2 \rightarrow i\text{-}C_4H_8 + HO_2$ (a)	$k_a=4x10^{-14}$	600-900K	5	52
	$\rightarrow i\text{-}C_4H_9O_2$ (b)	$k_b=2.7x10^{-5}/T^{2.7}$	<600K	3	52
45,4	$i\text{-}C_4H_9 + H \rightarrow C_4H_{10}$ (a)	$k_{a+b}=6x10^{-11}$		1.5	53
	$\rightarrow i\text{-}C_3H_7 + CH_3$ (b)	$k_c=1.5x10^{-12}$		2	53
	$\rightarrow i\text{-}C_4H_8 + H_2$ (c)	$\log k_b/k_{b+c}(N_2,1.0)=-8.253+$ $1.343x10^{-2}T-7.232x10^{-6}T^2+$ $1.344x10^{-9}T^3-2.777x10^{-14}T^4$			53
45,5	$i\text{-}C_4H_9 + O \rightarrow i\text{-}C_3H_7 + HCHO$ (a)	$k_{a+b}=1.6x10^{-10}$		3	55
	$\rightarrow i\text{-}C_3H_7CHO + H$ (b)	$k_b/k_a=3$			55
45,6	$i\text{-}C_4H_9 + OH \rightarrow C_4H_8 + H_2O$ (a)	$k_a=2x10^{-11}$		3	55
	$\rightarrow i\text{-}C_4H_9OH$ (b)	$k_b=4x10^{-11}$		3	55
45,7	$i\text{-}C_4H_9 + HO_2 \rightarrow i\text{-}C_3H_7 + HCHO + OH$	$4x10^{-11}$		2	56
45,8	$i\text{-}C_4H_9 + H_2O_2 \rightarrow i\ C_4H_{10} + HO_2$	$4.3x10^{-20}T^{2.13}exp(-1456/T)$		3 at 750K, 10 at 300K and 2500K	56
45,10	$i\text{-}C_4H_9 + CH_4 \rightarrow i\text{-}C_4H_{10} + CH_3$	$3.55x10^{-26}T^{3.72}exp(-4018/T)$		3	56
45,11	$i\text{-}C_4H_9 + C_2H_6 \rightarrow i\text{-}C_4H_{10} + C_2H_5$	$4.8x10^{-25}T^{3.7}exp(-4924/T)$		3	57
45,12	$i\text{-}C_4H_9 + HCHO \rightarrow i\text{-}C_4H_{10} + HCO$	$5x10^{-13}exp(-3270/T)$		3	57
45,15	$i\text{-}C_4H_9 + HCO \rightarrow i\text{-}C_4H_{10} + CO$	$6x10^{-11}$		1.5	58
45,16	$i\text{-}C_4H_9 + CH_3 \rightarrow i\text{-}C_5H_{12}$ (a)	$k_a=3.2x10^{-10}T^{-0.32}$		2	58
	$\rightarrow i\text{-}C_4H_8 + CH_4$ (b)	$k_b=1x10^{-11}T^{-0.32}$		2	58
45,17	$i\text{-}C_4H_9 + C_2H_5 \rightarrow i\text{-}C_4H_8 + C_2H_6$ (a)	$k_c=3.4x10^{-11}$		1.5	59
	$\rightarrow i\text{-}C_4H_{10} + C_2H_4$ (b)	$k_a=1.4x10^{-12}$		2.0	59
	$\rightarrow i\text{-}C_4H_9\text{-}C_2H_5$ (c)	$k_b=1.4x10^{-12}$		2.0	59
45,18	$i\text{-}C_4H_9 + C_2H_4 \rightarrow n\text{-}C_3H_7 + i\text{-}C_3H_7$	$< 5x10^{-14}exp(-3072/T)$		3	59
45,19	$i\text{-}C_4H_9 + C_2H_3 \rightarrow$ 4-methylpentene-1 (a)	$k_a=3.4x10^{-11}$		2	60
	$\rightarrow i\text{-}C_4H_8 + C_2H_4$ (b)	$k_b=1.4x10^{-12}$		4	60
	$\rightarrow i\text{-}C_4H_{10} + C_2H_2$ (c)	$k_c=1.4x10^{-12}$		4	60
45,20	$i\text{-}C_4H_9 + C_2H_2 \rightarrow C_3H_6 + C_3H_5$	$1.2x10^{-12}exp(-4531/T)$		3	60

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

No.	Reaction	Rate Constant $k/cm^3\ molecule^{-1}s^{-1}$	Uncertainty factor	Page
45,21	$i\text{-}C_4H_9 + C_2H \rightarrow$ 4-methylpentyne-1 (a)	$k_a=2x10^{-11}$	2	61
	$\rightarrow b_3H_3 + i\text{-}b_3H_7$ (b)	$k_b=1x10^{-11}$	3	61
45,22	$i\text{-}C_4H_9 + CH_3CO \rightarrow i\text{-}C_4H_9COCH_3$	$3.7x10^{-11}$	2	61
45,23	$i\text{-}C_4H_9 + CH_3OO \rightarrow i\text{-}C_3H_7 + CH_3O + HCHO$	$1.6x10^{-11}$	2	62
45,24	$i\text{-}C_4H_9 + CH_3O \rightarrow i\text{-}C_4H_{10} + H_2CO$ (a)	$k_a=2x10^{-11}$	3	62
	$\rightarrow i\text{-}C_4H_9OCH_3$ (b)	$k_b=1x10^{-11}$	3	62
45,25	$i\text{-}C_4H_9 + {}^1CH_2 \rightarrow i\text{-}C_3H_7 + C_2H_4$ (a)	$k_a=2.4x10^{-11}$	2	63
	$\rightarrow C_2H_5 + C_3H_6$ (b)	$k_b=7.2x10^{-11}$	2	63
	$\rightarrow CH_3 + i\text{-}C_4H_8$ (c)	$k_c=1.2x10^{-11}$	2	63
45,26	$i\text{-}C_4H_9 + {}^3CH_2 \rightarrow i\text{-}C_3H_7 + C_2H_4$	$3x10^{-11}$	2	63
45,38	$i\text{-}C_4H_9 + CH_3OH \rightarrow i\text{-}C_4H_{10} + CH_2OH$ (a)	$k_a=5.3x10^{-23}T^{3.17}exp(-4610/T)$	3	63
	$\rightarrow i\text{-}C_4H_{10} + CH_3O$ (b)	$k_b=2.4x10^{-23}T^{3.1}exp(-4510/T)$	3	63
45,39	$i\text{-}C_4H_9 + CH_2OH \rightarrow$ 3-methylbutanol (a)	$k_a=3.2x10^{-11}$	2	64
	$\rightarrow i\text{-}C_4H_{10} + CH_3O$ (b)	$k_b=3.2x10^{11}$	3	64
	$\rightarrow i\text{-}C_4H_{10} + CH_3O$ (c)	$k_c=0.8x10^{-12}$	3	64
45,40	$i\text{-}C_4H_9 + C_3H_8 \rightarrow i\text{-}C_4H_{10} + n\text{-}C_3H_7$ (a)	$k_a=1.5x10^{-24}T^{3.65}exp(-4600/T)$	3	64
	$\rightarrow i\text{-}C_4H_{10} + i\text{-}C_3H_7$ (b)	$k_b=2.5x10^{-24}T^{3.46}exp(-3750/T)$	3	64
45,41	$i\text{-}C_4H_9 + n\text{-}C_3H_7 \rightarrow n\text{-}C_3H_7 + i\text{-}C_4H_9$ (a)	$k_a=3.4x10^{-11}$	1.5	65
	$\rightarrow C_3H_6 + i\text{-}C_4H_{10}$ (b)	$k_b=2.4x10^{-12}$	2.0	65
	$\rightarrow i\text{-}C_4H_8 + C_3H_8$ (c)	$k_c=1.2x10^{-12}$	2.0	65
45,42	$i\text{-}C_4H_9 + i\text{-}C_3H_7 \rightarrow i\text{-}C_4H_9\text{-}i\text{-}C_3H_7$ (a)	$k_a=2.9x10^{-11}(300/T)^{0.35}$	2	65
	$\rightarrow i\text{-}C_4H_8 + i\text{-}C_3H_8$ (b)	$k_b=0.58x10^{-11}(300/T)^{0.35}$	2	65
	$\rightarrow i\text{-}C_4H_{10} + C_3H_6$ (c)	$k_c=0.32x10^{-11}(300/T)^{0.35}$	2	65
45,43	$i\text{-}C_4H_9 + i\text{-}C_4H_{10} \rightarrow i\text{-}C_4H_{10} + t\text{-}C_4H_9$	$0.9x10^{-24}T^{3.46}exp(-3\ 66/T)$	2.5	66
45,44	$i\text{-}C_4H_9 + t\text{-}C_4H_9 \rightarrow i\text{-}C_4H_9\text{-}t\text{-}C_4H_9$ (a)	$k_a=8.3x10^{-12}(300/T)^{0.75}$	2	66
	$\rightarrow i\text{-}C_4H_{10} + i\text{-}C_4H_8$ (b)	$k_b=5.0x10^{-12}(300/T)^{0.75}$	2	66
45,45	$i\text{-}C_4H_9 + i\text{-}C_4H_9 \rightarrow (i\text{-}C_4H_9)_2$ (a)	$k_a=1.7x10^{-11}$	1.5	66
	$\rightarrow i\text{-}C_4H_8 + i\text{-}C_4H_{10}$ (b)	$k_b=1.3x10^{-12}$	2.0	66

3. Chemical Kinetic Data Tables

43,1 $i\text{-}C_4H_{10} \rightarrow i\text{-}C_3H_7 + CH_3$

Reference	Conditions		Reaction rate constant, $k/cm^3molecule^{-1}s^{-1}$	Uncertainty factor
	Temp./K	[M] molecule cm^{-3}		
Koike, Morinaga (1982)	1300-1800	$2.5x10^{18}$ Ar 1.5-2% isobutane. Shock tube; UV detection of CH_3.	$6x10^{12}exp(-30614/T)s^{-1}$	2
Pratt, Rogers (1980)	973-1031	$6x10^{18}$ Ar 0.21% isobutane. Static "wall-less reactor"	$8.4x10^{15}exp(-42985/T)s^{-1}$	
Bradley (1974)	1200-1500	$3.5x10^{18}$ Ar 1% isobutane; single pulse shock tube.	$8.7x10^{9}exp(-24346/T)s^{-1}$	10
Konar, et al. (1973) calc.			$k\infty=6x10^{16}exp(-41130/T)s^{-1}$	
Tsang (1972) calc.			$k\infty=4x10^{16}exp(-41800/T)s^{-1}$	
Frey, Walsh (1969) calc.			$k\infty=5x10^{17}exp(-40000/T)s^{-1}$	
Konar, et al. (1968)	713-814	$1x10^{18}$ isobutane static system	$6x10^{17}exp(-41540/T)s^{-1}$	
Brooks(1966)	823-853	$2\text{-}7x10^{20}$ H_2, 5-20% isobutane. Flow reactor.	$7.9x10^{18}exp(-40280/T)s^{-1}$	
Recommended value			$k\infty=1.1x10^{26}T^{-2.61}exp(-45462/T)s^{-1}$	2
Recommended value			$logk/k\infty(N_2,1)=-2.047+5.196x10^{-3}T-3.765x10^{-6}T^2+6.442x10^{-10}T^3$	

Comments and Recommendations

The published rate expressions and rate constants vary widely. At common temperatures there are variations as large as factors of 100. All the calculations are based on the geometric mean rule for combination of unlike radicals. Except for the work of Tsang, they depend on the thermochemistry of the radicals and the combination rate. The results of Tsang are based on the decomposition rate of diisopropyl and ethane. The most "direct" and hence mechanistically straightforward study is the work of Koike and Morinaga. They monitored methyl radical formation. Their rate expression, which is based on methyl appearance, should be lowered by approximately a factor of 2 in order to take into account hydrogen atom attack on isobutane and the subsequent decomposition of the isobutyl radical to form another methyl. Experimental results and our recommendation are plotted in Figure 2.

We base our recommendations on our rate expressions for the combination of isopropyl (42,42) and methyl (16,16) radicals and the thermochemistry used in this evaluation. This leads to the high pressure rate expression $1.1x10^{26}T^{-2.61}exp(-45462/T)s^{-1}$. At 1100K it is in agreement with Tsang's calculated rate constants. With a 500 cm^{-1} step size down it reproduces the results of Koike and Morinaga. It is a factor of 10 larger than the measurements of Pratt and Rogers. The discrepencies from other calculated rate expressions are explicable in terms of changes in the thermochemistry. The high rate constants of Konar et al. and Brooks are probably due to contributions from radical chain processes. There are systematic errors in Bradley's measurements since we have noted a similar discrepancy in propane decomposition (40,1).

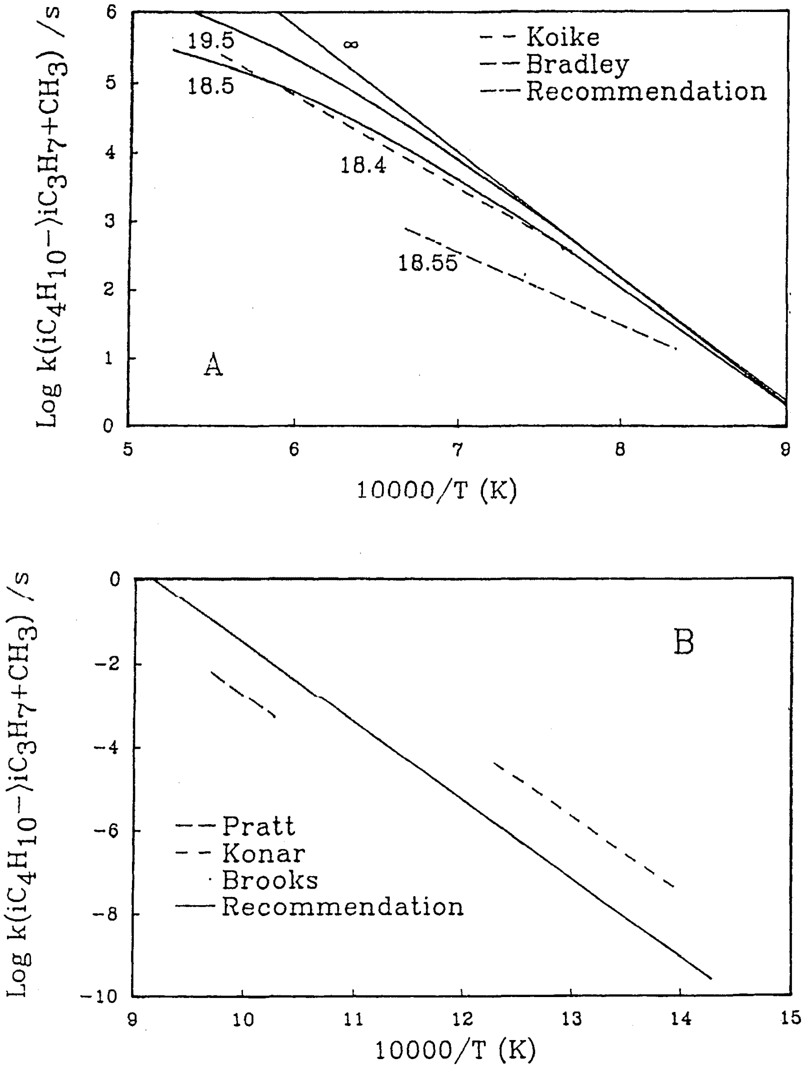

Fig. 2a and 2b. Previous results and current recommendations on isobutane decomposition

Fall-off behavior on the basis of a strong collision assumption can be found in Table A. Collision efficiencies as a function of temperature and step size down are tabulated in Table B. For a weak collider such as N_2 at 0.1, 1 and 10 atms and a step size down of 500 cm^{-1} we recommend the following expressions for k/k_∞ over the temperature range 800-2500 K. At lower temperatures, rate constants are at the high pressure limit.

$\log k/k_\infty(N_2,0.1) = -2.286 + 6.295\times10^{-3}T - 5.008\times10^{-6}T^2 + 9.254\times10^{-10}T^3$

$\log k/k_\infty(N_2,1) = -2.047 + 5.196\times10^{-3}T - 3.765\times10^{-6}T^2 + 6.442\times10^{-10}T^3$

$\log k/k_\infty(N_2,10) = -1.338 + 3.173\times10^{-3}T - 2.090\times10^{-6}T^2 - 3.038\times10^{-10}T^3$

With a polyatomic molecule such as isobutane a 1000 cm^{-1} step size down leads to the following expressions:

$\log k/k_\infty(i\text{-}C_4H_{10},0.1) = -2.091 + 5.497\times10^{-3}T - 4.153\times10^{-6}T^2 + 7.351\times10^{-10}T^3$

$\log k/k_\infty(i\text{-}C_4H_{10},1) = -1.577 + 3.857\times10^{-3}T - 2.656\times10^{-6}T^2 - 4.190\times10^{-10}T^3$

$\log k/k_\infty(i\text{-}C_4H_{10},10) = -0.804 + 1.816\times10^{-3}T - 1.092\times10^{-6}T^2 + 1.178\times10^{-10}T^3$

The uncertainty is a factor of 2.

Table A. $\log k/k_\infty$ as a function of temperature and pressure (strong collision)

log[M]	T/K 700	900	1100	1300	1500	1700	1900	2100	2300	2500
16.0	-0.02	-0.10	-0.29	-0.56	-0.89	-1.25	-1.64	-2.03	-2.41	-2.78
16.5		-0.05	-0.18	-0.38	-0.65	-0.96	-1.30	-1.66	-2.01	-2.35
17.0		-0.03	-0.10	-0.24	-0.45	-0.71	-1.00	-1.31	-1.63	-1.94
17.5		-0.01	-0.05	-0.14	-0.29	-0.49	-0.73	-1.00	-1.27	-1.55
18.0			-0.02	-0.07	-0.17	-0.32	-0.51	-0.72	-0.96	-1.19
18.5				-0.03	-0.09	-0.19	-0.33	-0.49	-0.68	-0.87
19.0				-0.01	-0.04	-0.10	-0.19	-0.31	-0.45	-0.60
19.5					-0.02	-0.05	-0.10	-0.17	-0.27	-0.38
20.0						-0.02	-0.04	-0.09	-0.14	-0.21
20.5							-0.02	-0.04	-0.07	-0.10
21.0								-0.01	-0.03	-0.04

Table B. Collision efficiency as a function of downward step size and temperature

T/K	Step-size (cm^{-1}) 150	300	600	1200	2400
700	2.78×10^{-2}	8.17×10^{-2}	1.98×10^{-1}	3.79×10^{-1}	5.81×10^{-1}
900	1.44×10^{-2}	4.58×10^{-2}	1.24×10^{-1}	2.72×10^{-1}	4.70×10^{-1}
1100	7.54×10^{-3}	2.55×10^{-2}	7.59×10^{-2}	1.87×10^{-1}	3.64×10^{-1}
1300	3.97×10^{-3}	1.41×10^{-2}	4.50×10^{-2}	1.23×10^{-1}	2.69×10^{-1}
1500	2.20×10^{-3}	8.04×10^{-3}	2.72×10^{-2}	8.04×10^{-1}	1.96×10^{-1}
1700	1.42×10^{-3}	5.28×10^{-3}	1.85×10^{-2}	5.83×10^{-2}	1.55×10^{-1}
1900	1.11×10^{-3}	4.18×10^{-3}	1.50×10^{-2}	4.93×10^{-2}	1.40×10^{-1}
2100	1.03×10^{-3}	3.91×10^{-3}	1.43×10^{-2}	4.81×10^{-2}	1.43×10^{-1}
2300	1.08×10^{-3}	4.12×10^{-3}	1.51×10^{-2}	5.19×10^{-2}	1.59×10^{-1}
2500	1.21×10^{-3}	4.64×10^{-3}	1.71×10^{-2}	5.92×10^{-2}	1.84×10^{-1}

(W. Tsang, May 1985)

References

Bradley, J. N., "The Mechanism for the High Temperature Pyrolysis of Alkenes. The Pyrolysis of Isobutane," Proc. Roy. Soc. A337, 199 (1974)

Brooks, C. T., "Gas Phase High Pressure Decomposition of Isobutane in the Presence of Hydrogen," Trans. Faraday Soc. 62, 935 (1966)

Frey, H. M., and Walsh, R., "The Thermal Unimolecular Reactions of Hydrocarbons," Chem. Rev. 69, 103 (1969)

Koike, T., and Morinaga, K., "UV Absorption Studies of the Pyrolysis of Isobutane in Shock Waves," Bull. Chem. Soc. Jpn. 55, 690 (1982)

Konar, R. S., Marshall, R. M., and Purnell, J. H., "Initiation of Isobutane Pyrolysis," Trans. Faraday Soc. 64, 405 (1968)

Konar, R. S., Marshall, R. M., and Purnell, J. H., "The Self Inhibited Pyrolysis of Isobutane," Int. J. Chem. Kinet. 5, 1007 (1973)

Pratt, G. L., and Rogers, D., "Wall-less Reaction Studies, Part 4 - Isobutane Pyrolysis," J. Chem. Soc. Faraday Trans. I 76, 1694 (1980)

Tsang, W., "Thermal Decomposition of 3,4-Dimethylhexane, 2,2,3-Trimethylpentane, Tert-Butylcyclohexene and Related Hydrocarbons," J. Phys. Chem. 76, 143 (1972)

43,3 $i\text{-}C_4H_{10} + O_2 \rightarrow HO_2 + i\text{-}C_4H_9$ **(a)**
$\rightarrow HO_2 + t\text{-}C_4H_9$ **(b)**

Reference	Conditions Temp./K	 [M] molecule cm^{-3}	Reaction rate constant, $k/cm^3molecule^{-1}s^{-1}$	Uncertainty factor
Walker (1975) review			$k_b=6.6x10^{-11}exp(-22140/T)$	2
Recommended value			$k_a=6.7x10^{-11}exp(-25630/T)$	10
Recommended value			$k_b=6.6x10^{-11}exp(-22140/T)$	3

Comments and Recommendations

There are no direct measurements on the rate constants for this process. Baldwin, Drewery and Walker (J. Chem. Soc., Faraday Trans. 1 80, 3195 (1984)) have reported recently the rate constant for O_2 abstraction of tertiary hydrogen from 2,3-dimethylbutane of $3.3x10^{-11}exp(-20820/T)$ $cm^3molecule^{-1}s^{-1}$, in good agreement with Walker's prediction. We therefore recommend the use of his rate expression with an uncertainty of a factor of 3. For abstraction of the primary hydrogen, k_a, we recommend his expression for ethane with an increase of a factor of 1.5 to take into account the extra hydrogens, i.e. $k_a = 6.7x10^{-11}exp(-25630/T)cm^3molecule^{-1}s^{-1}$, with an uncertainty of a factor of 10.

(W. Tsang, May 1985)

References

Walker, R. W., "A Critical Survey of Rate Constants for Reactions in Gas Phase Hydrocarbon Oxidation" in 'Reaction Kinetics" (P. G. Ashmore, Sr. Reptr.) Chemical Society, London, W1V0BN pg. 161, 1975

43,4 $i\text{-}C_4H_{10} + H \rightarrow i\text{-}C_4H_9 + H_2$ **(a)**
$\rightarrow t\text{-}C_4H_9 + H_2$ **(b)**

Reference	Conditions Temp./K	 [M] molecule cm^{-3}	Reaction rate constant, $k/cm^3molecule^{-1}s^{-1}$	Uncertainty factor
Baldwin, Walker (1979)			$k_a=3.3x10^{-10}exp(-4715/T)$	2 (753K)
review			$k_b = 0.85x10^{-10}exp(-3030/T)$	2 (753K)
Recommended value			$k_a=3.0x10^{-18}T^{2.54}exp(-3400/T)$	3
Recommended value			$k_b=1.0x10^{-18}T^{2.4}exp(-1300/T)$	3

Comments and Recommendations

The available literature has been reviewed by Baldwin and Walker. The rate expressions should be most accurate near 753 K. We have used their value at this temperature and scaled the result to fit the temperature dependence of the A-factor for the H + propane reaction. The resulting rate expressions are k_a=3.0x10^{-18}T$^{2.54}$exp(-3400/T)cm^{3}molecule^{-1}s^{-1} and k_b=1.0x10^{-18}T$^{2.4}$exp(-1300/T) cm^{3}molecule^{-1}s^{-1}. The uncertainty is a factor of 3.

(W. Tsang, May 1985)

References

Baldwin, R. R., and Walker, R. W., "Rate Constants for Hydrogen + Oxygen System, and for H Atoms and OH Radicals + Alkanes," J. Chem. Soc. Trans. I 75, 140 (1979)

43,5 $i\text{-}C_4H_{10} + O \rightarrow i\text{-}C_4H_9 + OH$ (a)

$\rightarrow t\text{-}C_4H_9 + OH$ (b)

Reference	Conditions Temp./K	 [M] molecule cm^{-3}	Reaction rate constant, k/cm^{3}molecule^{-1}s^{-1}	Uncertainty factor
Cohen, Westberg (1986)	300-2000		k_a=9.5x10^{-18}T$^{2.4}$exp(-2780/T)	2
review			k_b=3.55x10^{-19}T$^{2.5}$exp(-465/T)	2
Michael et al. (1983)	397-988		k_{a+b}=0.95x10^{-10}exp(-2654/T)	1.2
review				
Recommended value			k_a=7.1x10^{-19}T$^{2.5}$exp(-1834/T)	2
Recommended value			k_b=2.6x10^{-19}T$^{2.5}$exp(-560/T)	2

Comments and Recommendations

We have used the rate expression for isobutane of Michael et al., subtracted the contributions for primary hydrogen abstraction and thus obtained the contribution for tertiary hydrogen abstraction. We have then adjusted the rate expression to reflect a T$^{2.5}$ dependence of the A-factor. This leads to k_b=2.6x10^{-19}T$^{2.5}$exp(-460/T)cm^{3}molecule^{-1}s^{-1}. From the data given by Michael et al. on O attack on primary H-atom we obtain k_a = 7.1x10^{-19}T$^{2.5}$exp(-1734/T)cm^{3}molecule^{-1}s^{-1}. Over the entire temperature range we estimate an uncertainty of a factor of 2.

(W. Tsang, June 1986)

References

Cohen, N., and Westberg, K. R., "The Use of Transition-State Theory to Extrapolate Rate Coefficients for Reactions of O-Atoms with Alkanes," Int. J. Chem. Kinet. 18, 99 (1986).

Michael, J. V., Keil, D. G., and Klemm, R. B., "Theoretical Rate Constant Calculations for O(^{3}P) with Saturated Hydrocarbons," Int. J. Chem. Kinet. 15, 705 (1983)

43,6 $i\text{-}C_4H_{10} + OH \rightarrow i\text{-}C_4H_9 + H_2O$ (a)

$\rightarrow t\text{-}C_4H_{10} + H_2O$ (b)

Reference	Conditions Temp./K	 [M] molecule cm^{-3}	Reaction rate constant, $k/cm^3molecule^{-1}s^{-1}$	Uncertainty factor
Tully et al. (1986) (1986)	293-864	$(5\text{-}13)\times10^{18}$ He Laser photolysis of N_2O in presence of H_2O; LIF detection of OH. Reaction specificity from D labeling expts.	$k_a=3.81\times10^{-16}T^{1.53}\exp(-390/T)$ $k_b=9.52\times10^{-14}T^{0.51}\exp(-32/T)$	1.1 1.1
Walker (1985) review			$k_{a+b}=4.2\times10^{-16}T^{1.51}\exp(5/T)$	1.3
	300		$k_a/k_{a+b}=0.26$	1.2
	500		$k_a/k_{a+b}=0.48$	1.2
	750		$k_a/k_{a+b}=0.60$	1.2
	1000		$k_a/k_{a+b}=0.65$	1.2
Cohen (1983) review			$k_{a+b}=1.48\times10^{-20}T^{2.8}\exp(910/T)$ $k_a/k_b=14.8\exp(-1230/T)$	1.3 1.3
Recommended value			$k_a=3.81\times10^{-16}T^{1.53}\exp(-390/T)$	1.2
Recommended value			$k_b=9.52\times10^{-14}T^{0.51}\exp(-32/T)$	1.2

Comments and Recommendations

The work of Tully and coworkers is definitive. Their experimental results covered a wide temperature range and are in excellent agreement with all other measurements.

The results are summarized in Figure 3.

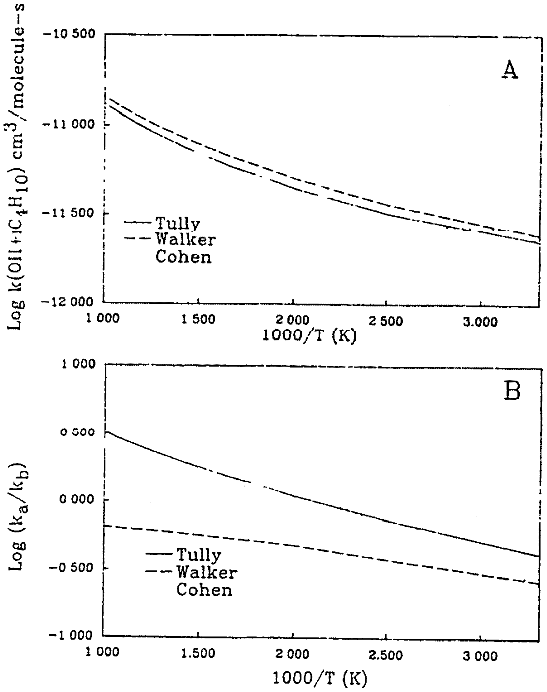

Fig. 3a and 3b. Previous results and current recommendations for OH attack on isobutane

(W. Tsang, June 1986)

References

Cohen, N., "The Use of Transition-State Theory to Extrapolate Rate Coefficients for Reactions of OH with Alkanes," Int. J. Chem. Kinet. 15, 503 (1983).

Tully, F. P., Goldsmith, J. E. M., and Droege, A. T., "Hydrogen-Atom Abstrtaction from Alkanes by OH. 4. Isobutane." J. Phys. Chem. **90**, 5932 (1986).

Walker, R. W., "Temperature Cefficients for Reactions of OH Radicals with Alkanes between 300 and 1000K", Int. J. Chem. Kinet. **17**, 573 (1985).

43,7 $i\text{-}C_4H_{10} + HO_2 \rightarrow i\text{-}C_4H_9 + H_2O_2$ **(a)**

$\rightarrow t\text{-}C_4H_9 + H_2O_2$ **(b)**

Reference	Conditions Temp./K	 [M] molecule cm^{-3}	Reaction rate constant, $k/cm^3molecule^{-1}s^{-1}$	Uncertainty factor
Walker (1976)	300-800		k_a=7.3x10^{-13}exp(-7520/T)	
review			k_b=8.1x10^{-14}exp(-5000/T)	
Walker (1974)	300-800		k_a=1.5x10^{-11}exp(-9750/T)	
review			k_b=1.66x10^{-12}exp(-7250/T)	
Recommended value			k_a=5x$10^{-20}T^{2.55}$exp(-7800/T)	2 at 750K,
Recommended value			k_b=6x$10^{-21}T^{2.55}$exp(-5300/T)	10 at 300
				and 2500K

Comments and Recommendations

The expressions given by Walker are based primarily on data near 750 K and estimates regarding temperature dependence. The most recent results for HO_2 + hexamethylethane reproduce the earlier assignment. [R.R. Baldwin, M.W.M. Hisham, A. Keen and R. W. Walker, J. Chem. Soc. Faraday Trans. I 71, 1165 (1982)]. We have based our recommendations on our BEBO transition state calculations on these expressions. This leads to:

$$k_a = 5.0\text{x}10^{-20}T^{2.55}\exp(-7800/T)cm^3molecule^{-1}s^{-1}$$

$$k_b = 6.0\text{x}10^{-21}T^{2.55}\exp(-5300/T)cm^3molecule^{-1}s^{-1}$$

The uncertainty is a factor of 2 near 750 K and increasing to a factor of 10 at the extremes of 300 and 2500 K.

(W. Tsang, June 1986)

References

Walker, R. W., "Rate Constants of Reactions in Gas Phase Hydrocarbon Oxidation," in "Gas Kinetics and Energy Transfer," Vol. 2 (P. G. Ashmore and R. J. Donovan, Sr. Reptrs.) Chem. Soc. Lond. W1V0BN pg. 296)

Walker, R. W., "A Critical Survey of Rate Constants for Reactions in Gas Phase Hydrocarbon Oxidation," in "Reaction Kinetics" Vol 1 (P.G. Ashmore, Sr. Reptr.) Chem. Soc. London W1V0BN pg. 161

43,15 $i\text{-}C_4H_{10} + HCO \rightarrow i\text{-}C_4H_9 + H_2CO$ (a)
$\rightarrow t\text{-}C_4H_9 + H_2CO$ (b)

Reference	Conditions		Reaction rate constant, $k/cm^3molecule^{-1}s^{-1}$	Uncertainty factor
	Temp./K	[M] molecule cm^{-3}		
Recommended value			$k_a=5.1x10^{-19}T^{2.5}exp(-9275/T)$	5
Recommended value			$k_b=5.7x10^{-20}T^{2.5}exp(-6800/T)$	5

Comments and Recommendations

There are no measurements for the rate constants of these processes. For the abstraction of primary hydrogens we recommend 1.5 times the rate expression for HCO attack on the primary hydrogens in propane, or

$k_a = 5.1x10^{-19}T^{2.5}exp(-9275/T)cm^3molecule^{-1}s^{-1}$

For abstraction of the tertiary hydrogen we reduce the A-factor by a factor of nine and the activation energy by $20kJmol^{-1}$. This leads to the expression

$k_b = 5.7x10^{-20}T^{2.5}exp(-6800/T)cm^3molecule^{-1}s^{-1}$

The uncertainties are a factor of 5.

(W. Tsang, October 1987)

43,16 $i\text{-}C_4H_{10} + CH_3 \rightarrow i\text{-}C_4H_9 + CH_4$ (a)
$\rightarrow t\text{-}C_4H_9 + CH_4$ (b)

Reference	Conditions		Reaction rate constant, $k/cm^3molecule^{-1}s^{-1}$	Uncertainty factor
	Temp./K	[M] molecule cm^{-3}		
Anastasi (1983)	478-560	$(1-2.2)x10^{17}$ acetone, $(1.6-3)x10^{18}$ isobutane; molecular modulation, spectrometric detection of CH_3 from acetone photolysis	$k_{a+b}=6.2x10^{-13}exp(-4404/T)$	1.5
Marshall, Shahkar (1983)	504-640	<1.5% azomethane in $(0.7-7)x10^{18}$ isobutane; static system	$k_{a+b}=2.6x10^{-11}exp(-6619/T)$	2
Kerr, Parsonage (1975) review	300-500		$k_{a+b}=1.4x10^{-13}exp(-4028/T)$	2
Konar et al. (1973)	770-855	$(2-20)x10^{18}$ isobutane	$k_a=2.4x10^{-11}exp(-8210/T)$ $k_b=5.4x10^{-12}exp(-6495/T)$	2 2
Recommended value			$k_a=2.25x10^{-24}T^{3.65}exp(-3600/T)$	2
Recommended value			$k_b=1.5x10^{-24}T^{3.46}exp(-2314/T)$	2

Comments and Recommendations

The most recent measurements yield rate constants that are factors of 2 to 3 larger than that recommended by Kerr and Parsonage. The latter summarizes scores of very straightforward exporiments. We have used their value for k_{a+b} as a base. For the abstraction of a primary hydrogen, k_a, we use the rate expression from propane (40,16) multiplied by 1.5 to take into account the extra hydrogens. This yields

$$k_a=2.25\times10^{-24}T^{3.65}\exp(-3600/T)\mathrm{cm}^3\mathrm{molecule}^{-1}\mathrm{s}^{-1}$$

and goes smoothly through the results of Konar et al. We then derive the rate expression for the abstraction of a tertiary hydrogen by subtraction from k_{a+b} with the temperature dependence of the preexponential factor which we used for the abstraction of a secondary hydrogen in propane (40,16). This leads to

$$k_b=1.5\times10^{-24}T^{3.46}\exp(-2314/T)\mathrm{cm}^3\mathrm{molecule}^{-1}\mathrm{s}^{-1}$$

A plot of the data and our recommendations can be found in Figure 4. The estimated uncertainty is a factor of 2.

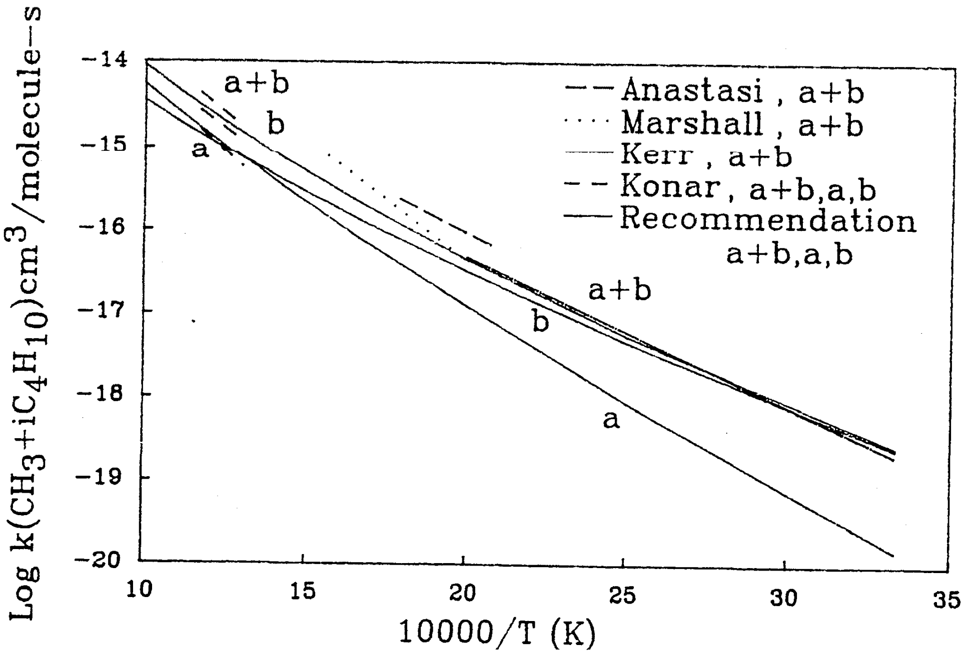

Fig. 4. Experimental data and current recomendations for methyl - isobutane reaction.

References

Anastasi, C., "Study of the Methyl Isobutane Reaction in the Range 478<T < 560," J. Chem. Soc. Faraday Trans. I 79, 741 (1983)

Kerr, J. A., and Parsonage, M. J., "Evaluated Kinetic Data on Gas Phase Hydrogen Transfer Reactions of Methyl Radicals," (Butterworths, London, 1970) 40

Konar, R. S., Marshall, R. M., and Purnell, J. H., J. Chem. Soc. Faraday Trans. I 79, 1983 (1983).

Marshall, R. M., and Shahkar, G., "The Molecular Component in the Thermal Decomposition of Azomethane," J. Chem. Soc. Faraday Trans. I 79, 1891 (1983).

43,17 $i\text{-}C_4H_{10} + C_2H_5 \rightarrow C_2H_6 + i\text{-}C_4H_9$ (a)
$\rightarrow C_2H_6 + t\text{-}C_4H_9$ (b)

Reference	Conditions Temp./K	Conditions [M] molecule cm^{-3}	Reaction rate constant, $k/cm^3molecule^{-1}s^{-1}$	Uncertainty factor
Boddy, Steacie (1960)	323-573	photolysis of pentanone-d_6 $(6\text{-}15)\times10^{11}$ in $(2.5\text{-}6)\times10^{17}$ isobutane	$k_{a+b}=5\times10^{-14}\exp(-4480/T)$	1.4
Recommended value			$k_a=2.3\times10^{-24}T^{3.65}\exp(-4600/T)$	2.5
Recommended value			$k_b=0.9\times10^{-24}T^{3.46}\exp(-3000/T)$	2.5

Comments and Recommendations

The measurement of Boddy and Steacie is with deuterated ethyl radicals and is referenced against the combination rate constant. We have derived the rate constant given above using $k_r(C_2D_5)=1.7\times10^{-11}cm^3molecule^{-1}s^{-1}$. We have used Boddy and Steacie's result for C_2D_5 attack on neopentane and the functional dependence of the A-factor for methyl attack on the primary bonds on isobutane to obtain

$k_a=2.3\times10^{-24}T^{3.65}\exp(-4600/T)cm^3molecule^{-1}s^{-1}$

We then derived the following rate expression

$k_b=0.9\times10^{-24}T^{3.46}\exp(-3000/T)cm^3molecule^{-1}s^{-1}$

for ethyl attack on the tertiary hydrogen by trying to reproduce the experimental k_{a+b} value, using k_a and the $T^{3.46}$dependence of the A-factor from methyl attack on the tertiary hydrogen. The uncertainty is a factor of 2.5.

(W. Tsang, June 1986)

References

Boddy, P. J., and Steacie, E. W. R., "Hydrogen Atom Abstraction by Ethyl-d_5 Radical. Part I.," Can. J. Chem. 38, 1576 (1960).

43,19 $i\text{-}C_4H_{10} + C_2H_3 \rightarrow C_2H_4 + i\text{-}C_4H_9$ (a)
$\rightarrow C_2H_4 + t\text{-}C_4H_9$ (b)

Reference	Conditions Temp./K	Conditions [M] molecule cm^{-3}	Reaction rate constant, $k/cm^3molecule^{-1}s^{-1}$	Uncertainty factor
Recommended value			$k_a=2.25\times10^{-24}T^{3.65}\exp(-2600/T)$	5
Recommended value			$k_b=1.5\times10^{-24}T^{3.46}\exp(-1314/T)$	5

Comments and Recommendations

There are no measurements on the rate constants for this reaction. Since the C-H bond energy is about 20 $kJmol^{-1}$ higher than that for methyl, we recommend rate expressions similar to that for $CH_3+i\text{-}C_4H_{10}$ (43,16) except for a ~ 8.5 $kJmol^{-1}$ decrease in activation energy. This leads to:

$k_a=2.25\times10^{-24}T^{3.65}\exp(-2600/T)cm^3molecule^{-1}s^{-1}$

$k_b=1.5\times10^{-24}T^{3.46}\exp(-1314/T)cm^3molecule^{-1}s^{-1}$

The uncertainty is a factor of 5.

(W. Tsang, June 1986)

43,21 $i-C_4H_{10} + C_2H \rightarrow i-C_4H_9 + C_2H_2$ (a)

$\rightarrow t-C_4H_9 + C_2H_2$ (b)

Reference	Conditions Temp./K	 [M] molecule cm^{-3}	Reaction rate constant, $k/cm^3molecule^{-1}s^{-1}$	Uncertainty factor
Recommended value			$k_a=1x10^{-11}$	3
Recommended value			$k_b=1.1x10^{-12}$	3

Comments and Recommendations

There have been no measurements on the rate constants for these processes. We recommend for the abstraction of the primary hydrogen atom 1.5 times the rate constant for C_2H attack on C_2H_6 (21,10) or

$$k_a = 1.0x10^{-11}cm^3molecule^{-1}s^{-1}.$$

For the tertiary hydrogen we estimate

$$k_b = 1.1x10\ ^{12}cm^3molecule^{-1}s^{-1}.$$

The uncertainty is a factor of 3.

(W. Tsang, June 1986)

43,22 $i-C_4H_{10} + CH_3CO \rightarrow i-C_4H_9 + CH_3CHO$ (a)

$\rightarrow t-C_4H_9 + CH_3CHO$ (b)

Reference	Conditions Temp./K	 [M] molecule cm^{-3}	Reaction rate constant, $k/cm^3molecule^{-1}s^{-1}$	Uncertainty factor
Recommended value			$k_a=5.1x10^{-19}T^{2.5}exp(-9275/T)$	10
Recommended value			$k_b=5.7x10^{-20}T^{2.5}exp(-6800/T)$	10

Comments and Recommendations

There are no measurements for the rate constants of these reactions. The rate expressions should be very close to that for formyl radical on isobutane. We recommend

$$k_a=5.1x10^{-19}T^{2.5}exp(-9275/T)cm^3molecule^{-1}s^{-1}$$

$$k_b=5.7x10^{-20}T^{2.5}exp(-6800/T)cm^3molecule^{-1}s^{-1}$$

The uncertainties are factors of 10.

(W. Tsang, June 1986)

43,23 $i\text{-}C_4H_{10} + CH_3O_2 \rightarrow i\text{-}C_4H_9 + CH_3O_2H$ (a)
$\rightarrow t\text{-}C_4H_9 + CH_3O_2H$ (b)

	Conditions			
Reference	Temp./K	[M] molecule cm^{-3}	Reaction rate constant, $k/cm^3molecule^{-1}s^{-1}$	Uncertainty factor
Parkes (1975)	298	$2x10^{19}$ isobutanes, 1.5% azomethane, 2% oxygen	$k_a=4x10^{-20}$	
Recommended value			$k_a=5x10^{-20}T^{2.55}exp(-7800/T)$	2 at 750K, 10 at 300K and 2500K
Recommended value			$k_b=6x10^{-21}T^{2.55}exp(-5300/T)$	2 at 750K, 10 at 300K and 2500K

Comments and Recommendations

There is very little experimental information on these processes. We recommend our rate expressions for the HO_2 abstraction reaction:

$k_a=5x10^{-20}T^{2.55}exp(-7800/T)cm^3molecule^{-1}s^{-1}$
$k_b=6x10^{-21}T^{2.55}exp(-5300/T)cm^3molecule^{-1}s^{-1}$

The uncertainty is a factor of 2 near 750K and a factor of 10 at the extremes of 300K and 2500K. Note that our expression for k_a is in satisfactory agreement with Alcock and Mile's result for CH_3O_2 attack on 2,3-dimethylbutane, although it is much smaller than Parke's results at room temperature. The general situation for peroxide radical reactions is very confusing. (W. G. Alcock and B. Mile, Combust. Flame 24, 12 (1975).
(W. Tsang, June 1986)

References

Parkes, D. A., "The Role of Alkylperoxy and Alkoxy Radicals in Alkyl Radical Oxidation at Room Temperatures," Symp. Combust. 15, (Combustion Institute, Pittsburgh, 1975) 795.

43,24 $i\text{-}C_4H_{10} + CH_3O \rightarrow i\text{-}C_4H_9 + CH_3OH$ (a)
$\rightarrow t\text{-}C_4H_9 + CH_3OH$ (b)

	Conditions			
Reference	Temp./K	[M] molecule cm^{-3}	Reaction rate constant, $k/cm^3molecule^{-1}s^{-1}$	Uncertainty factor
Berces, Trotman-Dickenson (1961)	463-563	$(1-2)x10^{17}$ isobutane, copyrolysis with dimethyl and di-t-butyl peroxide	$k_{a+b}=1.7x10^{-13}exp(-2064/T)$	5
Recommended value			$k_a=0.8x10^{-12}exp(-3676/T)$	5 at 400-600K, 10 at 300 and 1500K
Recommended value			$k_b=3.8x10^{-14}exp(-1446/T)$	

Comments and Recommendations

Using the rate constants determined for CH_3O + neopentane by Shaw and Trotman-Dickenson (Shaw and Trotman-Dickenson, J. Chem. Soc., 3210 (1060)) as characteristic for the abstraction of primary hydrogens, we recommend:

$$k_a=0.8x10^{-12}exp(-3676/T)cm^3molecule^{-1}s^{-1}$$

Substracting this from the reported rate expression for the CH_3O reaction with isobutane leads to

$$k_b=3.8x10^{-14}exp(-1446/T)cm^3molecule^{-1}s^{-1}$$

These experiments appear to be difficult and we estimate the uncertainty as a factor of 5 over applicable temperature ranges and an order of magnitude at 300 and 1500 K. We have also reduced the pre-exponential factors by a factor of 2 due to the correction of an arithmetic error by Kerr and Parsonage (Kerr and Parsonage, "Handbook of Bimolecular and Termolecular Gas Reactions," CRC Press, Inc., Boca Raton, Florida, pg. 286).

(W. Tsang, October 1987)

References

Berces, T., and Trotman-Dickenson, A. J., "The Reactions of Methoxy Radicals with Cyclopropane and Isobutane," J. Chem. Soc., 348 (1961).

Shaw, R., and Trotman-Dickenson, A. F., "The Reactions of Methoxy Radicals with Alkanes," J. Chem. Soc., 3210 (1960).

43,25 $i\text{-}C_4H_{10} + {}^3CH_2 \rightarrow i\text{-}C_4H_9 + CH_3$ **(a)**

$\rightarrow t\text{-}C_4H_9 + CH_3$ **(b)**

$\rightarrow i\text{-}C_4H_{10} + {}^1CH_2$ **(c)**

	Conditions		Reaction rate constant	Uncertainty
Reaction/Reference	T range/K	[M] range/cm^3	k/$cm^3molecule^{-1}s^{-1}$	factor
Bohland et al (1985) (reanalysis of earlier work)	296-698		k_a=1.61x10^{-11}Exp(-3970/T) k_b=1.81x10^{-12}Exp(-2467/T)	1.3 1.3
Bohland et al (1985)	298	3x10^{14} CH_2CO 1 to 10x10^{15} $i\text{-}C_4H_{10}$ in 3.4x10^{16} He	k_{-c}/k_{-total}=0.28	1.3
Dobe et al (1985)	296-705	2-8x10^{14} CH_2CO 1-10x10^{15} $i\text{-}C_4H_{10}$ in 1.5-7x10^{16} He	k_{a+b}=1.15x10^{-11}Exp(-3090 T)	1.3
Recommended Value			k_a=1.61x10^{-11}Exp(-3970/T) k_b=1.81x10^{-12}Exp(-2467/T) k_c=3.7x10^{-11}exp(-4481/T)	1.3 300-700K increasing to 5 at 2500K

Comments and Reccomendations:

The laser magnetic resonance work involving the direct detection of the triplet methylene must be considered definitive. It is interesting that the rate constants are considerably faster than the comparable methyl radical reactions. We recommend the values deduced by Bohland and coworkers (1) for the abstraction process.

$$k_a=1.61\text{x}10^{-11}\text{Exp}(-3970/T)\ \text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$$
$$k_b=1.81\text{x}10^{-12}\text{Exp}(-2467/T)\ \text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$$

For the conversion of triplet to singlet we use the number deduced by Bohland and coworkers (2) for the reverse and through the equilibrium constant find,

$$k_c=3.7\text{x}10^{-11}\text{Exp}(-4481/T)\ \text{cm}^3\text{molecule}^{-1}\text{s}^{-1}\text{-}$$

The uncertainty over the experimental temperature range is quoted by the investigators. We assign an uncertainty of a factor of 5 at 2500 K to account for the possibility of curvature in the Arrhenius expression of the same order as for methyl abstraction.
(W. Tsang. June 1986)

References:

Dobe, S., Bohland, T., Temps, F., and Wagner, H. G., "A Direct Study of the Reactions of $CH_2(X^3B_1)$-Radicals with Selected Hydrocarbons in the Temperature Range 296 K ≤ T ≤ 795 K.," Ber. Bunsenges. Phys. Chem. **89**, 432, 1985

Bohland, T., Dobe, S., Temps, F., and Wagner, H. G., "Kinetics of the Reactions between $CH_2(X^3B_1)$-Radicals and Saturated Hydrocarbons in the Temperature Range 296 T 707 K, Ber. Bunsenges. Phys Chem. **89**, 432, 19852, 1985

Bohand, T., Temps, F., and Wagner, H. G., ""The Contributions of Intersystem Crossing and Reaction in the Removal of $CH_2(aA_1)$ by Hydrocarbons Studied with LMR," Ber. Bunsenges. Phys. Chem. **89**, 1013, 19855

43,26 $\textbf{i-C}_4\textbf{H}_{10} + {}^1\textbf{CH}_2 \rightarrow \textbf{C}_2\textbf{H}_5 + \textbf{i-C}_3\textbf{H}_7$ **(a)**
$\rightarrow \textbf{CH}_3 + \textbf{t-C}_4\textbf{H}_9$ **(b)**
→ **isopentane** **(c)**
→ **neopentane** **(d)**
$\rightarrow {}^3\textbf{CH}_2 + \textbf{i-C}_4\textbf{H}_{10}$ **(e)**

Reference	Conditions Temp./K	 [M] molecule cm^{-3}	Reaction rate constant, $k/\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$	Uncertainty factor
Bohland et al (1985)	298	$3\text{x}10^{14}$ CH_2CO		
		1 to $10\text{x}10^{15}$ i-C_4H_{10}	$k_e/k_{a+b+c+d+e} = 0.28$	1.3
		in $3.4\text{x}10^{16}$ He		
Halberstadt and Crump (1972/1973)	300	$3\text{-}25\text{x}10^{18}$;	$k_{a+b}/k({}^1CH_2+CH_4)=3.9$	1.3
		ketene photolysis in	$k_b/k_a=0.15$	1.3
		ethane and isobutane	(limiting high P values)	
Recommended value			$k_{a+c}{}^{\infty}=2\text{x}10^{-10}$	2
Recommended value			$\log k_a/k_{a+c}(N_2,1.0)=-11.904+$ $1.913\text{x}10^{-2}T-1.082\text{x}10^{-5}T^2+$ $2.461\text{x}10^{-9}T^3-1.724\text{x}10^{-13}T^4$	
Recommended value			$k_{b+d}{}^{\infty}=3\text{x}10^{-11}$	
			$k_e=9.010^{-11}$	1.3

Comments and Recommendations

There are no direct measurements for the rate constant of this process. Combination of the measurement of Halberstadt and Crump, Bohland et al., and our recommendation for $^1CH_2+CH_4$ (25,10) leads to

$k_{a+c}=2x10^{-10}cm^3molecule^{-1}s^{-1}$,$k_{b+d}=3x10^{-11}cm^3molecule^{-1}s^{-1}$, and $k_e=9x10^{-10}cm^3molecule^{-1}s^{-1}$

It is clear that insertion into the primary C-H bond is the main reaction. These are values at the high pressure limit.

Under high pressure combustion conditions the chemically activated molecules can also fragment. Our RRKM calculations, on a strong collision basis, for the decomposition of the hot isopentane, the main initial product, can be found in Table A. Below 700 K stabilization is the main process. Collision efficiency, as a function of temperature and step size down, can be found in Table B. Uncertainties are factors of 2.

Table A. Log of fractional decomposition (log k_a/k_{a+c}) of isopentane following $^1CH_2$ insertion into the primary bonds of isobutane as a function of temperature and pressure.

log[M]	T/K									
	700	900	1100	1300	1500	1700	1900	2100	2300	2500
16.0	-1.07	-0.54	-0.23	-0.09	-0.04	-0.01	-0.00	-0.00	-0.00	-0.00
17.0	-1.95	-1.19	-0.65	-0.33	-0.16	-0.07	-0.03	-0.02	-0.01	-0.00
18.0	-2.92	-2.07	-1.35	-0.84	-0.50	-0.29	-0.16	-0.09	-0.05	-0.03
19.0	-3.92	-3.05	-2.27	-1.64	-1.15	-0.79	-0.53	-0.35	-0.24	-0.16
20.0	-4.92	-4.04	-3.25	-2.59	-2.04	-1.59	-1.23	-0.95	-0.73	-0.56
21.0	-5.92	-5.04	-4.25	-3.58	-3.02	-2.55	-2.16	-1.83	-1.55	-1.32

Table B. Collision efficiency $\beta(e)$ for isopentane decomposition as a function of temperature and step size down

T/K	Step-size (cm^{-1})				
	150	300	600	1200	2400
700	$2.54x10^{-2}$	$7.57x10^{-2}$	$1.86x10^{-1}$	$3.63x10^{-1}$	$5.66x10^{-1}$
900	$1.31x10^{-2}$	$4.21x10^{-2}$	$1.16x10^{-1}$	$2.58x10^{-1}$	$4.54x10^{-1}$
1100	$6.75x10^{-3}$	$2.31x10^{-2}$	$6.95x10^{-2}$	$1.74x10^{-1}$	$3.47x10^{-1}$
1300	$3.43x10^{-3}$	$1.22x10^{-2}$	$3.97x10^{-2}$	$1.10x10^{-1}$	$2.49x10^{-1}$
1500	$1.76x10^{-3}$	$6.49x10^{-3}$	$2.22x10^{-2}$	$6.73x10^{-2}$	$1.70x10^{-1}$
1700	$9.67x10^{-4}$	$3.63x10^{-3}$	$1.29x10^{-2}$	$4.16x10^{-2}$	$1.15x10^{-1}$
1900	$5.60x10^{-4}$	$2.13x10^{-3}$	$7.75x10^{-3}$	$2.60x10^{-2}$	$7.63x10^{-2}$
2100	$3.26x10^{-4}$	$1.25x10^{-3}$	$4.61x10^{-3}$	$1.58x10^{-2}$	$4.85x10^{-2}$
2300	$1.82x10^{-4}$	$7.01x10^{-4}$	$2.60x10^{-3}$	$9.05x10^{-3}$	$2.84x10^{-2}$
2500	$9.52x10^{-5}$	$3.66x10^{-4}$	$1.36x10^{-3}$	$4.74x10^{-3}$	$1.50x10^{-2}$

At 0.1, 1 and 10 atmosphere pressure of N_2 and over the temperature range of 700-1500K we recommend

$\log(\text{fractional decomp.}, N_2, 0.1) = -12.251 + 2.518\text{x}10^{-2}T - 1.922\text{x}10^{-5}T^2 + 6.449\text{x}10^{-9}T^3 - 8.030\text{x}10^{-13}T^4$

$\log(\text{fractional decomp.}, N_2, 1.0) = -11.904 + 1.913\text{x}10^{-2}T - 1.082\text{x}10^{-5}T^2 + 2.461\text{x}10^{-9}T^3 - 1.724\text{x}10^{-13}T^4$

$\log(\text{fractional decomp.}, N_2, 10.0) = -9.374 + 7.565\text{x}10^{-3}T + 1.815\text{x}10^{-6}T^2 - 2.797\text{x}10^{-9}T^3 + 5.847\text{x}10^{-13}T^4$

where we have assumed 500 cm^{-1} as the step size down. For isopentane as the third body and with a 1000 cm^{-1}step size down, we obtain over the temperature range 700-1500 K

$\log(\text{fractional decomp.}, C_5H_{12}, 0.1) = -11.736 + 2.163\text{x}10^{-2}T - 1.473\text{x}10^{-5}T^2 + 4.387\text{x}10^{-9}T^3 - 4.823\text{x}10^{-13}T^4$

$\log(\text{fractional decomp.}, C_5H_{12}, 1.0) = -10.069 + 1.213\text{x}10^{-2}T - 3.503\text{x}10^{-6}T^2 - 5.317\text{x}10^{-10}T^3 + 2.552\text{x}10^{-13}T^4$

$\log(\text{fractional decomp.}, C_5H_{12}, 10.0) = -8.048 + 2.815\text{x}10^{-3}T + 5.938\text{x}10^{-6}T^2 - 4.148\text{x}1^{-9}T^3 + 7.321\text{x}10^{-13}T^4$

Below 700 K under these conditions the hot adduct is stabilized. Above 1500 K decomposition is the primary process. The overall uncertainty is a factor of 3.

(W. Tsang, October 1987)

References

Halberstadt, M. L., and Crump, J., "Insertion of Methylene into the Carbon-Hydrogen Bonds of the C_1 to C_4 Alkanes," J. Photochem. **1**, 295 (1972/1973).

Bohland, T., Temps, F., and Wagner, H. G., "The Contributions of Intersystem Crossing and Reaction in the Removal o $CH_2(aA_1)$ by Hydrocarbons Studied with LMR," Ber. Bunseges. Phys. Chem. **89**, 432 (1985)

43,39 $\mathbf{i\text{-}C_4H_{10} + CH_2OH \rightarrow i\text{-}C_4H_9 + CH_3OH}$ **(a)**
$\mathbf{\rightarrow t\text{-}C_4H_9 + CH_3OH}$ **(b)**

Reference	Conditions		Reaction rate constant, $k/cm^3molecule^{-1}s^{-1}$	Uncertainty factor
	Temp./K	[M] molecule cm^{-3}		
Recommended value			$k_a=5\text{x}10^{-22}T^{2.95}\exp(-7033/T)$	5
Recommended value			$k_b=2\text{x}10^{-22}T^{2.76}\exp(-5433/T)$	5

Comments and Recommendations

There are no data on the rate constants for these reactions. For the abstraction of a primary hydrogen we recommend 1.5 times the rate expression for hydroxymethyl attack on the primary hydrogens in propane or

$k_a=5\text{x}10^{-22}T^{2.95}\exp(-7033/T)cm^3molecule^{-1}s^{-1}$

For the tertiary hydrogen, we have derived a rate expression based on the relative rate of C_2H_5 on the primary and tertiary hydrogens in $i\text{-}C_4H_{10}$ or

$k_b=2\text{x}10^{-22}T^{2.76}\exp(-5433/T)cm^3molecule^{-1}s^{-1}$

The uncertainty is a factor of 5.

(W. Tsang, October 1987)

43,41 $i\text{-}C_4H_{10} + n\text{-}C_3H_7 \rightarrow i\text{-}C_4H_9 + C_3H_8$ (a)
$\rightarrow t\text{-}C_4H_9 + C_3H_8$ (b)

Reference	Conditions Temp./K	 [M] molecule cm^{-3}	Reaction rate constant, $k/cm^3molecule^{-1}s^{-1}$	Uncertainty factor
Recommended value			$k_a=2.3\times10^{-24}T^{3.65}\exp(-4600/T)$	3
Recommended value			$k_b=0.9\times10^{-24}T^{3.46}\exp(-3000/T)$	3

Comments and Recommendations

There are no measurements on the rate constants for this reaction. However, there can be little doubt that the rate expression will equal that for ethyl radical attack on isobutane (43,17). We therefore recommend:

$$k_a=2.3\times10^{-24}T^{3.65}\exp(-4600/T)cm^3molecule^{-1}s^{-1}$$
$$k_b=0.9\times10^{-24}T^{3.46}\exp(-3000/T)cm^3molecule^{-1}s^{-1}$$

The uncertainty is a factor of 3.

(W. Tsang, June 1986)

43,42 $i\text{-}C_4H_{10} + i\text{-}C_3H_7 \rightarrow i\text{-}C_4H_9 + C_3H_8$ (a)
$\rightarrow t\text{-}C_4H_9 + C_3H_8$ (b)

Reference	Conditions Temp./K	 [M] molecule cm^{3}	Reaction rate constant, $k/cm^3molecule^{-1}s^{-1}$	Uncertainty factor
Recommended value			$k_a=2.1\times10^{-26}T^{4.2}\exp(-4386/T)$	3
Recommended value			$k_b=2.5\times10^{-27}T^{4.2}\exp(-3000/T)$	5

Comments and Recommendations

There are no measurements on the rate constants of these reactions. We recommend, for the abstraction of a primary hydrogen 1.5 times the rate expression for isopropyl attack on ethane (42,11) or

$$k_a=2.1\times10^{-26}T^{4.2}\exp(-4386/T)cm^3molecule^{-1}s^{-1}$$

For the tertiary hydrogen, we have reduced the pre-exponential factor by a factor of nine to take into account the reaction degeneracy and the activation energy by 12 $kJmol^{-1}$. This leads to the rate expression

$$k_b=2.5\times10^{-27}T^{4.2}\exp(-3000/T)cm^3molecule^{-1}s^{-1}$$

The uncertainties are a factor of 3 and 5 respectively.

(W. Tsang, October 1987)

44,1 $t\text{-}C_4H_9 \rightarrow i\text{-}C_4H_8 + H$ (a)
$\rightarrow C_3H_6 + CH_3$ (b)

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, $k/cm^3 molecule^{-1} s^{-1}$	Uncertainty factor
Tsang (1985) (review)	300-800		$k_a=8.3\times10^{13}\exp(-19376/T)s^{-1}$	3
Canosa and Marshall (1981)	584-604	$8.5\text{-}45\times10^{17}$ isobutane; pyrolysis of small quantities of azomethane	$k_a=4.7\times10^{14}\exp(-19840/T)s^{-1}$	3
Tsang (1964)	1000-1100	$6\text{-}26\times10^{18}$ Argon; single pulse shock tube	$k_a/k_b=0.03$	
Birell and Trotman-Dickenson (1960)	663-800	5.3×10^{17}; pivaldehyde photolysis	$k_a=8.5\times10^{14}\exp(-20860/T)s^{-1}$	2.5
Recommended value			$k_a=8.3\times10^{13}\exp(-19200/T)s^{-1}$ $\log k/k_\infty(N_2,1)=-0.305+1.595\times10^{-3}T-2.045\times10^{-6}T^2+4.169\times10^{-10}T^3$	3

Comments and Recommendations

The recommended rate expression is very close to that given in the earlier review. The activation energy has been slightly lowered to match better the experimental results. It is consistent with the rate constants for decomposition given above and for the reverse H-atom addition reaction as given by Harris and Pitts (G. W. Harris and J. N. Pitts, Jr., J. Chem. Phys., 77, 3995, (1982)) and a heat of formation of t-butyl radical of ~52 kJ mol^{-1}. Reaction channel b involves 1,2 isomerization followed by methyl ejection and is unimportant. RRKM calculations assuming strong collisions lead to k/k_∞ ratios as given in Table A. Collision efficiency as a function of temperature and step size down can be found in Table B. k/k_∞ ratios for N_2 assuming a 500 cm^{-1} step size down, at 0.1, 1 and 10 atm, are as follows:

$$\log k/k_\infty(N_2,0.1) = -1.326 + 6.134\times10^{-3}T - 8.640\times10^{-6}T^2 + 3.666x^{-9}T^3 - 5.347\times10^{-13}T^4$$
$$\log k/k_\infty(N_2,1) = -0.305 + 1.595\times10^{-3}T - 2.045\times10^{-6}T^2 + 4.169\times10^{-10}T^3$$
$$\log k/k_\infty(N_2,10) = -0.413 + 1.465\times10^{-3}T - 1.404\times10^{-6}T^2 + 2.463\times10^{-10}T^3$$

For a polyatomic such as isobutane a 1000 cm^{-1} step size, at 0.1, 1 and 10 atm, leads to:

$$\log k/k_\infty(C_4H_{10},0.1) = -1.195 + 5.096\times10^{-3}T - 6.636\times10^{-6}T^2 + 2.647\times10^{-9}T^3 - 3.698\times10^{-13}T^4$$
$$\log k/k_\infty(C_4H_{10},1) = -0.309 + 1.570\times10^{-3}T - 1.662\times10^{-6}T^2 + 3.082\times10^{-10}T^3$$
$$\log k/k_\infty(C_4H_{10},10) = -0.299 + 9.591\times10^{-4}T - 8.133\times10^{-7}T^2 + 1.148\times10^{-10}T^3$$

These relations should be applicable from 700-1500 K. Below this temperature the reaction is effectively at the high pressure limit. The uncertainty is a factor of 3.

Figure 5 contains Arrhenius plots of the experimental values of rate constants for the unimolecular reactions of t-butyl radicals and our recommended values.

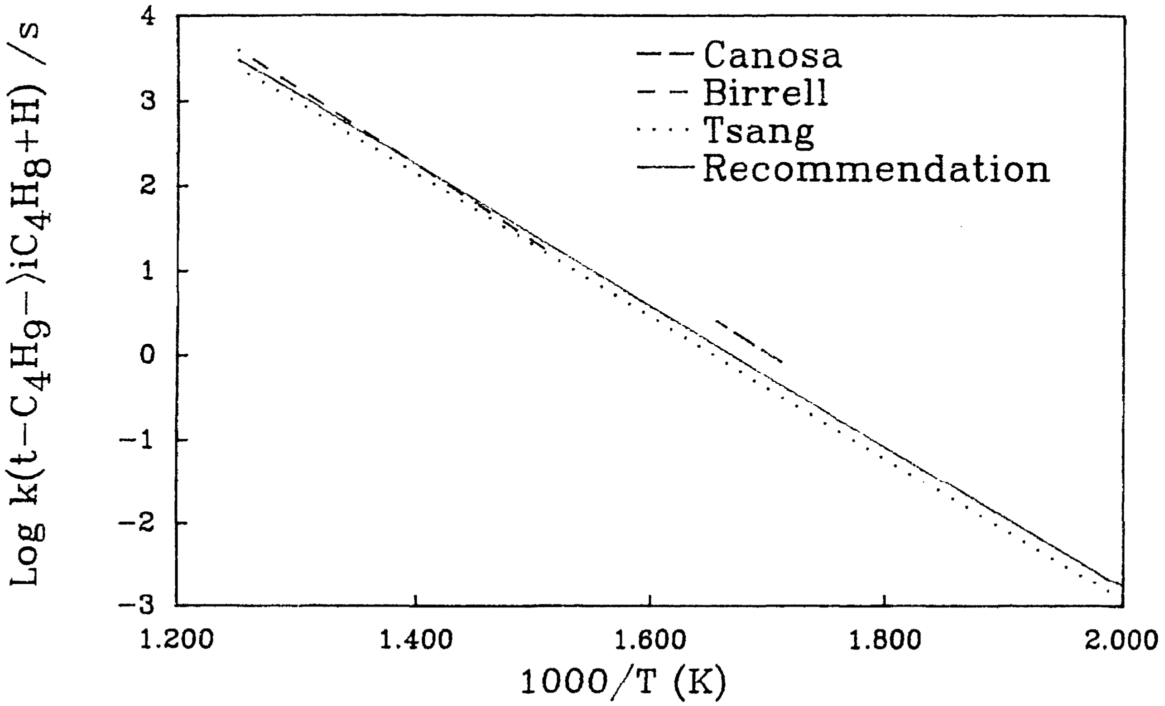

Fig. 5. Previous Results and Current Recommendations on t-Butyl Decomposition

Table A. $\log k/k_\infty$ as a function of temperature and concentration for strong collisions

log[M]	T/K										
	500	700	900	1100	1300	1500	1700	1900	2100	2300	2500
16.0	-0.13	-0.41	-0.82	-1.29	-1.77	-2.24	-2.67	-3.07	-3.43	-3.73	-3.99
16.5	-0.06	-0.26	-0.58	-0.97	-1.40	-1.82	-2.23	-2.60	-2.94	-3.24	-3.50
17.0	-0.03	-0.15	-0.38	-0.70	-1.06	-1.43	-1.80	-2.15	-2.47	-2.76	-3.01
17.5	-0.01	-0.08	-0.23	-0.47	-0.76	-1.08	-1.40	-1.72	-2.01	-2.28	-2.52
18.0		-0.03	-0.13	-0.29	-0.51	-0.76	-1.04	-1.31	-1.58	-1.83	-2.05
18.5		-0.01	-0.06	-0.16	-0.31	-0.50	-0.72	-0.95	-1.18	-1.40	-1.60
19.0			-0.02	-0.08	-0.17	-0.30	-0.46	-0.64	-0.82	-1.00	-1.18
19.5				-0.03	-0.08	-0.16	-0.26	-0.39	-0.52	-0.66	-0.80
20.0				-0.01	-0.03	-0.07	-0.13	-0.21	-0.30	-0.39	-0.50
20.5					-0.01	-0.03	-0.06	-0.10	-0.15	-0.20	-0.27
21.0						-0.01	-0.02	-0.04	-0.06	-0.09	-0.12

Table B. Collision efficiency β(e) as a function of downward step size and temperature

T/K	Step-size (cm^{-1})				
	150	300	600	1200	2400
500	$4.56x10^{-2}$	$1.24x10^{-1}$	$2.71x10^{-1}$	$4.69x10^{-1}$	$6.61x10^{-1}$
700	$1.85x10^{-2}$	$5.74x10^{-2}$	$1.50x10^{-1}$	$3.11x10^{-1}$	$5.13x10^{-1}$
900	$7.86x10^{-3}$	$2.66x10^{-2}$	$7.88x10^{-2}$	$1.93x10^{-1}$	$3.74x10^{-1}$
1100	$4.14x10^{-3}$	$1.47x10^{-2}$	$4.74x10^{-2}$	$1.31x10^{-1}$	$2.92x10^{-1}$
1300	$3.05x10^{-3}$	$1.12x10^{-2}$	$3.78x10^{-2}$	$1.13x10^{-1}$	$2.80x10^{-1}$
1500	$2.95x10^{-3}$	$1.10x10^{-2}$	$3.81x10^{-2}$	$1.19x10^{-1}$	$3.19x10^{-1}$
1700	$3.33x10^{-3}$	$1.24x10^{-2}$	$4.38x10^{-2}$	$1.40x10^{-1}$	$3.91x10^{-1}$
1900	$3.99x10^{-3}$	$1.49x10^{-2}$	$5.25x10^{-2}$	$1.69x10^{-1}$	$4.81x10^{-1}$
2100	$4.80x10^{-3}$	$1.79x10^{-2}$	$6.27x10^{-2}$	$2.01x10^{-1}$	$5.73x10^{-1}$
2300	$5.67x10^{-3}$	$2.10x10^{-2}$	$7.32x10^{-2}$	$2.33x10^{-1}$	$6.60x10^{-1}$
2500	$6.52x10^{-3}$	$2.41x10^{-2}$	$8.34x10^{-2}$	$2.63x10^{-1}$	$7.39x10^{-1}$

(W. Tsang, May 1985)

References

Birrell, R. N., and Trotman-Dickenson, A. F., "The Reactions of Alkyl Radicals. Part VII. t-Butyl Radicals from the Photolysis of Pivaldehyde," J. Chem. Soc., 4218 (1980)

Canosa, C. E., and Marshall, R. M., "The Rate Constant for $t-C_4H_9 \rightarrow H + i-C_4H_8$ and the Thermodynamics Parameters of $t-C_4H_9$," Int. J. Chem. Kinet. 13, 303 (1981)

Tsang, W., "The Stability of Alkyl Radicals," J. Am. Chem. Soc. 107, 2872 (1985)

Tsang, W., "Thermal Decomposition of Hexamethylethane, 2,2,3-Trimethylbutane and Neopentane in a Single Pulse Shock Tube", J. Chem. Phys. 44, 4283 (1966).

44,2 $t-C_4H_9 + H_2 \rightarrow i-C_4H_{10} + H$

	Conditions		Reaction rate constant,	Uncertainty
Reference	Temp./K	[M]/molecule cm^{-3}	$k/cm^3molecule^{-1}s^{-1}$	factor
log $K_p = -0.8174 + 2989.8/T + 478130/T^2 - 5.7677x10^7/T^3$				
Recommended value			$3.07x10^{-26}T^{4.24}exp(-4510/T)$	3

Comments and Recommendations

There are no measurements for the rate constants of this process. We recommend the following rate expression which is based on detailed balance and the rate expression for the reverse process (43,4)

$3.07x10^{-26}T^{4.24}exp(-4510/T)cm^3molecule^{-1}s^{-1}$.

We estimate the uncertainty to be a factor of 3.

(W. Tsang, May 1986)

44,3 $t\text{-}C_4H_9 + O_2 \rightarrow i\text{-}C_4H_8 + HO_2$

Reference	Conditions		Reaction rate constant, $k/cm^3molecule^{-1}s^{-1}$	Uncertainty factor
	Temp./K	$[M]/molecule\ cm^{-3}$		
Evans and Walker (1979)	713-813	$6x10^{18}$ N_2 and H_2 with traces of O_2 and hexamethylethane in KCl coated pyrex vessel and gas chromatographic analysis	$k/k_{44,2}=0.35exp(-7449/T)$	1.5
Recommended value			$8x10^{-13}$	3

Comments and Recommendations

There are no uncertainties regarding the reaction mechanism. We have combined our recommendations for rate expression for t-butyl attack on H_2 (44,2) at 750 K (i.e. $3.8x10^{-12}exp(-7785/T)$) with the results of Evans and Walker to obtain at 753 K

$$k = 1.3x10^{-12}exp(-336/T)cm^3molecule^{-1}s^{-1}$$

or, at 753 K, $k=8.3x10^{-13}cm^3molecule^{-1}s^{-1}$, which is in substantial agreement with the result of $7.6x10^{-13}cm^3molecule^{-1}s^{-1}$ from the work of Evans and Walker. We recommend an average of the two values over all temperature range, since recent results on similar type of reactions suggest if anything a negative temperature dependence. The uncertainty limit is a factor of 3.

(W. Tsang, October 1987)

References

Evans, G. A., and Walker, R. W., "Reactions of t-Butyl Radicals with Hydrogen and Oxygen," J.C.S. Faraday I 79, 1458 (1979).

44,4 $t\text{-}C_4H_9 + H \rightarrow i\text{-}C_4H_8 + H_2$ (a)

$\rightarrow i\text{-}C_4H_{10}$ (b)

$\rightarrow i\text{-}C_3H_7 + CH_3$ (c)

Reference	Conditions		Reaction rate constant, $k/cm^3molecule^{-1}s^{-1}$	Uncertainty factor
	Temp./K	$[M]/molecule\ cm^{-3}$		
Recommended value			$k_a=9x10^{-12}$	2
Recommended value			$k_{b+c}=4x10^{-11}$	2
Recommended value			$logk_c/k_{b+c}=-10.882+1.893x10^{-2}T-1.191x10^{-5}T^2+3.183x10^{-9}T^3-2.999x10^{-13}T^4$	

Comments and Recommendations

There are no measurements on the rate constants for these reactions. From related systems fairly good estimates can be made. Reaction (a) is a disproportionation process. Following the similar reaction for ethyl + H (17,4), we recommend $k_a = 9x10^{-12}$ $cm^3molecule^{-1}s^{-1}$ with an uncertainty of a factor of 2. Reactions (b) and (c) are related since the hot adduct can either stabilize (b) or decompose (c). Due to the latter channel, the overall rate constant, which we estimate to be $4\times10^{-11}\mathrm{cm^3 molecule^{-1} s^{-1}}$ with an uncertainty of a factor of 2, is not pressure dependent.

Fractional decomposition as a function of temperature and pressure, on the assumption of strong collisions can be found in Table A. Collision efficiency on a per collision basis can be found in Table B.

For temperatures in excess of 700 K our best estimates for the decomposition to stabilization plus decomposition ratio at 0.1, 1 and 10 atm. are given in the following relations. We have assumed in one case N_2 as the weak collider and a step-size down of 500 $\mathrm{cm^{-1}}$ and in the other case isobutane as the weak collider and a step size down of 1000 $\mathrm{cm^{-1}}$. Above 1500 K, decomposition is the only process.

$$\log k_c/k_{b+c}(N_2,0.1) = -10.543 + 2.260\times10^{-2}T - 1.796\times10^{-5}T^2 + 6.265\times10^{-9}T^3 - 8.089\times10^{-13}T^4$$
$$\log k_c/k_{b+c}(N_2,1) = -10.882 + 1.893\times10^{-2}T - 1.191\times10^{-5}T^2 + 3.183\times10^{-9}T^3 - 2.999\times10^{-13}T^4$$
$$\log k_c/k_{b+c}(N_2,10) = -10.375 + 1.280\times10^{-2}T - 4.027\times10^{-6}T^2 + 3.673\times10^{-10}T^3 + 2.380\times10^{-13}T^4$$
$$\log k_c/k_{b+c}(i\text{-}C_4H_{10},0.1) = -10.359 + 2.014\times10^{-2}T - 1.453\times10^{-5}T^2 + 4.610\times10^{-9}T^3 - 5.427\times10^{-13}T^4$$
$$\log k_c/k_{b+c}(i\text{-}C_4H_{10},1) = -10.223 + 1.506\times10^{-2}T - 7.358\times10^{-6}T^2 + 1.203\times10^{-9}T^3 - 5.386\times10^{-15}T^4$$
$$\log k_c/k_{b+c}(i\text{-}C_4H_{10},10) = -9.833 + 9.738\times10^{-3}T - 9.928\times10^{-7}T^2 - 1.446\times10^{-9}T^3 + 3.661\times10^{-13}T^4$$

These values are subject to an uncertainty of a factor of 2.

Table A. logk(decomp.)/(k(decomp. + stab.) as a function of concentration and temperature

log[M]	T/K										
	500	700	900	1100	1300	1500	1700	1900	2100	2300	2500
16.0	-1.62	-0.80	-0.37	-0.16	-0.06	-0.02	-0.01				
16.5	-2.08	-1.14	-0.58	-0.27	-0.12	-0.05	-0.02	-0.01			
17.0	-2.56	-1.53	-0.85	-0.44	-0.21	-0.10	-0.04	-0.02	-0.01		
17.5	-3.05	-1.98	-1.19	-0.66	-0.35	-0.18	-0.09	-0.04	-0.02	-0.01	-0.01
18.0	-3.55	-2.45	-1.58	-0.96	-0.55	-0.31	-0.17	-0.09	-0.05	-0.02	-0.01
18.5	-4.05	-2.94	-2.02	-1.32	-0.82	-0.50	-0.29	-0.17	-0.10	-0.06	-0.03
19.0	-4.55	-3.43	-2.49	-1.73	-1.16	-0.76	-0.48	-0.30	-0.19	-0.12	-0.07
19.5	-5.05	-3.93	-2.98	-2.19	-1.56	-1.09	-0.75	-0.51	-0.34	-0.23	-0.16
20.0	-5.55	-4.43	-3.48	-2.67	-2.01	-1.49	-1.09	-0.79	-0.57	-0.41	-0.30
20.5	-6.05	-4.93	-3.98	-3.16	-2.49	-1.93	-1.49	-1.14	-0.88	-0.67	-0.52
21.0	-6.55	-5.43	-4.48	-3.66	-2.98	-2.41	-1.95	-1.57	-1.26	-1.03	-0.84

Table B. Collision efficiency $\beta(e)$ as a function of downward step size and temperature

T/K	Step-size (cm^{-1})				
	150	300	600	1200	2400
500	$5.81x10^{-2}$	$1.51x10^{-1}$	$3.13x10^{-1}$	$5.15x10^{-1}$	$6.98x10^{-1}$
700	$2.90x10^{-2}$	$8.48x10^{-2}$	$2.03x10^{-1}$	$3.86e10^{-1}$	$5.88x10^{-1}$
900	$1.53x10^{-2}$	$4.86x10^{-2}$	$1.31x10^{-1}$	$2.82x10^{-1}$	$4.81x10^{-1}$
1100	$8.31x10^{-3}$	$2.79x10^{-2}$	$8.20x10^{-2}$	$1.98x10^{-1}$	$3.80x10^{-1}$
1300	$4.51x10^{-3}$	$1.59x10^{-2}$	$5.00x10^{-2}$	$1.34x10^{-1}$	$2.87x10^{-1}$
1500	$2.47x10^{-3}$	$8.98x10^{-3}$	$3.00x10^{-2}$	$8.71x10^{-2}$	$2.08x10^{-1}$
1700	$1.42x10^{-3}$	$5.28x10^{-3}$	$1.83x10^{-2}$	$5.69x10^{-2}$	$1.48x10^{-1}$
1900	$8.66x10^{-4}$	$3.27x10^{-3}$	$1.17x10^{-2}$	$3.79x10^{-2}$	$1.06x10^{-1}$
2100	$5.49x10^{-4}$	$2.09x10^{-3}$	$7.60x10^{-3}$	$2.55x10^{-2}$	$7.50x10^{-2}$
2300	$3.50x10^{-4}$	$1.34x10^{-3}$	$4.93x10^{-3}$	$1.69x10^{-2}$	$5.15x10^{-2}$
2500	$2.19x10^{-4}$	$8.41x10^{-4}$	$3.11x10^{-3}$	$1.08x10^{-2}$	$3.36x10^{-2}$

(W. Tsang, May 1985)

44,5 $t\text{-}C_4H_9 + O \rightarrow i\text{-}C_4H_8 + OH$ (a)
$\rightarrow CH_3COCH_3 + CH_3$ (b)

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, k/$cm^3molecule^{-1}s^{-1}$	Uncertainty factor
Washida, Bayes (1980)	298±4	$1x10^{17}$ Isobutane O and O_2	$k_{a+b}=8.7x10^{-10}$ $k_a/k_b=4$	2
Hoyermann, Sievert (1978)	300	$1x10^{16}$ He	$k_b>k_a$	
Recommended value			$k_a=3x10^{-10}$	3
Recommended value			$k_a/k_b=1$	4

Comments and Recommendations

The experimental results are widely divergent. The recent results of Slagle et al. on O + C_2H_5 (Slagle, I. R., Sarzynski, D., Gutman, D., Miller, J. A., and Melius, C. F., J. Chem. Soc., Faraday Trans. 2, submitted) are in disagreement with Hoyermann and Sievert's observations on that system and calls into question their results (listed above). The total rate constant measured by Washida and Bayes seems to be extraordinarily large. It is, for example, an order of magnitude larger than that for H + C_2H_5. Our recommendation is strongly influenced by the results of Slagle et al. and uses Washida and Bayes' results as an upper limit.

(W. Tsang, October 1987)

References

Hoyermann, K., and Sievert, R., "The Reactions of Alkyl Radicals with Oxygen Atoms: Identification of Primary Products at Low Pressure," Symp. Combust. 17, (Combustion Institute, Pittsburgh, 1979) 517

Washida, N., and Bayes, K. D., "Reactions of Isobutane and the tert-Butyl Radical with Atomic and Molecular Oxygen," J. Phys. Chem. 84, 1309 (1980)

44,6 $t\text{-}C_4H_9 + OH \rightarrow i\text{-}C_4H_8 + H_2O$

Reference	Conditions		Reaction rate constant, k/cm^{3}molecule^{-1}s^{-1}	Uncertainty factor
	Temp./K	[M]/molecule cm^{-3}		
Recommended value			3×10^{-11}	3

Comments and Recommendations

Although there are no measurements on the rate constants for this reaction, there can be little question of the reaction mechanism, since under combustion conditions abstraction as well as addition to form the hot t-butanol will lead to the same products. We therefore recommend a rate constant of 3×10^{-11}cm^{3}molecule^{-1}s^{-1} with an uncertainty of a factor of 3.

(W. Tsang, April 1986)

44,7 $t\text{-}C_4H_9 + HO_2 \rightarrow CH_3 + CH_3COCH_3 + OH$

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

Comments and Recommendations

Although there are no measurements on the rate constant for this process, there can be little doubt that the predominant process will be addition with a rate constant approximately 3×10^{-11}cm^3-molecule^{-1}s^{-1} followed by rapid decomposition of the adduct. The estimated uncertainty is a factor of 2.

(W. Tsang, May 1986)

44,8 $t\text{-}C_4H_9 + H_2O_2 \rightarrow HO_2 + C_4H_{10}$

Reference	Conditions		Reaction rate constant, k/cm^{3}molecule^{-1}s^{-1}	Uncertainty factor
	Temp./K	[M]/molecule cm^{-3}		
$\log K_p = -0.610 + 1081.76/T + 374976/T^2 - 4.818 \times 10^7/T^3$				
Recommended value			$4.2 \times 10^{-26} T^{3.79} \exp(-136/T)$	5

Comments and Recommendations

Although the rate constants for this process have not been measured, the equilibrium constant and rate expression for the reverse reaction (43,7) give $k = 4.2 \times 10^{-26} T^{3.79} \exp(-136/T)$cm^{3}molecule^{-1}s^{-1}. The uncertainty is a factor of 5.

(W. Tsang, May 1986)

44,10 $t\text{-}C_4H_9 + CH_4 \rightarrow i\text{-}C_4H_{10} + CH_3$

	Conditions		Reaction rate constant,	Uncertainty
Reference	Temp./K	[M]/molecule cm^{-3}	$k/cm^3molecule^{-1}s^{-1}$	factor
$\log K_p = 0.693 - 3177/T + 4.445x10^5/T^2 - 5.053x10^7/T^3$				
Recommended value			$8.2x10^{-31}T^{5.38}exp(-5996/T)$	3

Comments and Recommendations

There are no direct measurements on the rate constant for this process. However, from the equilibrim constant and the rate expression for the reverse reaction we obtain $8.2x10^{-31}T^{5.38}exp(-5996/T)cm^3molecule^{-1}s^{-1}$. We estimate an uncertainty of a factor of 3.

(W. Tsang, May 1086)

44,11 $t\text{-}C_4H_9 + C_2H_6 \rightarrow i\text{-}C_4H_{10} + C_2H_5$

	Conditions		Reaction rate constant,	Uncertainty
Reference	Temp./K	[M]/molecule cm^{-3}	$k/cm^3molecule^{-1}s^{-1}$	factor
$\log K_p = 1.009 - 2154.9/T + 439464/T^2 - 5.2724x10^7/T^3$				
Recommended value			$5.6x10^{-30}T^{5.17}exp(-4563/T)$	3

Comments and Recommendations

There are no measurements on the rate constants for this process. From the reverse reaction and the thermodynamics we obtain $5.6x10^{-30}T^{5.17}exp(-4563/T)cm^3molecule^{-1}s^{-1}$. We estimate the uncertainty as a factor of 3.

(W. Tsang, May 1985)

44,12 $t\text{-}C_4H_9 + HCHO \rightarrow i\text{-}C_4H_{10} + HCO$

	Conditions		Reaction rate constant,	Uncertainty
Reference	Temp./K	[M]/molecule cm^{-3}	$k/cm^3molecule^{-1}s^{-1}$	factor
Recommended value			$5.4x10^{-15}exp(-1788/T)$	5

Comments and Recommendations

Although there are no measurements on the rate constants for this process, we believe that the rate constant for t-butyl attack on pivaldehyde (Birrell, R. N., and Trotman-Dickenson, A. F., J. Chem. Soc., 4218 (1960)) will be quite similar to that for this reaction. Therefore, we recommend the rate expression $5.4x10^{-15}exp(-1788/T)cm^3molecule^{-1}s^{-1}$, where we have taken into account the number of aldehydic hydrogens and the rate constant for the t-butyl combination used here (44,44). The uncertainty is a factor of 5.

(W. Tsang, May 1985)

44,15 $t\text{-}C_4H_9 + HCO \rightarrow i\text{-}C_4H_{10} + CO$ (a)
$\rightarrow t\text{-}C_4H_9CHO$ (b)

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, $k/cm^3molecule^{-1}s^{-1}$	Uncertainty factor
Recommended value			k_a=1x10^{-10}	5
Recommended value			k_b=2x10^{-11}	5

Comments and Recommendations

There are no measurements on the rate constants for this reaction. We recommend rate constants slightly smaller than that for methyl radicals or $k_a = 1x10^{-10}cm^3molecule^{-1}s^{-1}$, $k_b = 2x10^{-11}$ $cm^3molecule^{-1}s^{-1}$. The uncertainty is a factor of 5.

(W. Tsang, April 1986)

44,16 $t\text{-}C_4H_9 + CH_3 \rightarrow i\text{-}C_4H_8 + CH_4$ (a)
$\rightarrow neo\text{-}C_5H_{12}$ (b)

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, $k/cm^3molecule^{-1}s^{-1}$	Uncertainty factor
Anastasi, Arthur	308	2.8x10^{18} N_2	k_b=2.1x10^{-11}	2
(1980)		0.4x10^{18} azoisobutane 1.6x10^{18} azomethane photolysis with molecular modulation spectroscopic detection	k_a/k_b=0.84	1.2
Gibian, Corley (1973) review			k_a/k=0.7	1.2
Recommended value			k_a=2.1x10^{-11}(300/T)	2
Recommended value			k_b=2.7x10^{-11}(300/T)	2

Comments and Recommendations

The geometric mean rule for the combination of t-butyl and methyl yields

$$k_b = 2.7x10^{-11}(300/T)cm^3molecule^{-1}s^{-1}$$

and is in substantial agreement with the results of Anastasi and Arthur. The disproportionation to combination ratio is in the expected range.

(W. Tsang, October 1987)

References

Anastasi, C., and Arthur, N. L., "Rate Constants for the Reactions of CH_3 Radicals with C_2H_5, $i\text{-}C_3H_7$ and $t\text{-}C_4H_9$ Radicals," J. Chem. Soc., Faraday Trans. 2 83, 277 (1987).

Gibian, M. J., and Corley, R. C., "Organic Radical-Radical Reactions - Disproportionation vs Combination," Chem. Rev. 13, 441 (1973)

44,17 $t\text{-}C_4H_9 + C_2H_5 \rightarrow i\text{-}C_4H_{10} + C_2H_4$ (a)
$\rightarrow i\text{-}C_4H_8 + C_2H_6$ (b)
$\rightarrow CH_3C(CH_3)_2CH_2CH_3$ (c)

	Conditions		Reaction rate constant,	Uncertainty
Reference	Temp./K	[M]/molecule cm^{-3}	$k/cm^3molecule^{-1}s^{-1}$	factor
Gibian, Corley (1973)	300		$k_a/k_c=0.32$	1.15
review	300		$k_b/k_c=0.52$	1.15
Recommended value			$k_a=0.51\times10^{-11}(300/T)^{0.75}$	2
Recommended value			$k_b=0.83\times10^{-11}(300/T)^{0.75}$	2
Recommended value			$k_c=1.6\times10^{-11}(300/T)^{0.75}$	2

Comments and Recommendations

The disproportionation to combination ratio given in the review of Gibian and Corley should have an uncertainty of 15%. Although there have been no measurements on the combination rate constant, the geometric mean rule will lead to $k_c=1.6\times10^{-11}(300/T)^{0.75}cm^3molecule^{-1}s^{-1}$ with an uncertainty of a factor of 2.

(W. Tsang, May 1986)

References

Gibian, M. J., and Corley, R. C., "Organic Radical-Radical Reactions. Disproportionation vs Combination," Chem. Rev. 13, 441 (1973)

44,18 $t\text{-}C_4H_9 + C_2H_4 \rightarrow (CH_3)_3CCH_2CH_2$ (a)
$\rightarrow i\text{-}C_4H_8 + C_2H_5$ (b)
$\rightarrow C_5H_{10} + CH_3$ (c)

	Conditions		Reaction rate constant,	Uncertainty
Reference	Temp./K	[M]/molecule cm^{-3}	$k/cm^3molecule^{-1}s^{-1}$	factor
Birrell, Trotman-Dickenson (1960)	300-650	5.3×10^{17}. Pivaldehyde photolysis	$k_a=6.3\times10^{-15}\exp(-3190/T)$	2
Recommended value			$k_{b+c}=4.8\times10^{-15}\exp(-3190/T)$	3
Recommended value			$k_b/k_c=0.5\exp(1200/T)$	1.5

Comments and Recommendations

The measurement of Birrell and Trotman-Dickenson is for the addition process. (We have adjusted their values in order to make them consistent with our combination rate of t-butyl (44,44)). Under combustion conditions it will be readily reversed. However, the possibility of 1,4 H-transfer will lead to the formation of the 2,2-dimethylbutyl-1 radical. Its prime modes of decomposition are the reactions given above.

We suggest the use of the expression $4.8\times10^{-15}\exp(-3190/T)cm^3molecule^{-1}s^{-1}$ for k_{b+c} with an uncertainty factor of 3. k_b/k_c should be taken as equal to $0.5\exp(1200/T)$ with an uncertainty factor of 1.5
(W. Tsang, April 1986)

References

Birrell, R. N., and Trotman-Dickenson, A. F., "The Reactions of Alkyl Radicals. Part VII. t-Butyl Radicals from the Photolysis of Pivaldehyde," J. Chem. Soc., 4218 (1960).

44,19 $t\text{-}C_4H_9 + C_2H_3 \rightarrow i\text{-}C_4H_8 + C_2H_4$ (a)

$\rightarrow i\text{-}C_4H_{10} + C_2H_2$ (b)

$\rightarrow C_6H_{12}$ (c)

$\rightarrow C_5H_9 + CH_3$ (d)

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, $k/cm^3molecule^{-1}s^{-1}$	Uncertainty factor
Recommended value			$k_{(c+d)\infty}=1.6x10^{-11}(300/T)^{0.75}$	3
Recommended value			$log[k_d/k_{c+d}(N_2,1)]=-10.083+1.745x10^{-2}T-1.060x10^{-5}T^2+2.601x10^{-9}T^3-2.033x10^{-13}T^4$	5
Recommended value			$k_b=0.83x10^{-11}(300/T)^{0.75}$	3
Recommended value			$k_a=0.51x10^{-11}(300/T)^{0.75}$	3

Comments and Recommendations

There are no measurements on the rate constants for these processes. We suggest using the rate expressions for ethyl + t-butyl for reactions (a), (b), and (c) + (d). Thus

$k_{c+d} = 1.6x10^{-11}(300/T)^{0.75}cm^3molecule^{-1}s^{-1}$

$k_a/k_{c+d} = 0.32$

$k_b/k_{c+d} = 0.52$

The estimated uncertainty is a factor of 3. The branching ratio between k_c(stabilization) and k_d(decomposition) is pressure dependent. On the basis of a strong collision assumption and with itself as the collider, ratio of decomposition to stabilization + decomposition can be found in Table A. For weak colliders, Table B gives collision efficiencies β(e) as a function of temperature and step size down. In the case of N_2 and 2,2-dimethylbutene-1 as weak colliders with step size down of 500 cm^{-1} and 1000 cm^{-1} at 0.1, 1 and 10 atm, the decomposition to stabilization + decomposition ratios are given in the following expressions:

$logk_d/k_{c+d}(N_2,0.1) = -9.804 + 2.154x10^{-2}T - 1.741x10^{-5}T^2 + 6.136x10^{-9}T^3 - 7.972x10^{-13}T^4$

$logk_d/k_{c+d}(N_2,1) = -10.083 + 1.745x10^{-2}T - 1.060x10^{-5}T^2 + 2.601x10^{-9}T^3 - 2.033x10^{-13}T^4$

$logk_d/k_{c+d}(N_2,10) = -9.205 + 9.834x10^{-3}T - 7.643x10^{-7}T^2 - 1.919x10^{-9}T^3 + 4.971x10^{-13}T^4$

and

$logk_d/k_{c+d}(C_6H_{12},0.1) = -9.532 + 1.887x10^{-2}T - 1.369x10^{-5}T^2 + 4.319x10^{-9}T^3 - 5.006x10^{-13}T^4$

$logk_d/k_{c+d}(C_6H_{12},1) = -9.175 + 1.279x10^{-2}T - 5.082x10^{-6}T^2 + 1.507x10^{-10}T^3 + 1.700x10^{-13}T^4$

$logk_d/k_{c+d}(C_6H_{12},10) = -8.339 + 5.760x10^{-3}T + 3.416x10^{-6}T^2 \quad 3.515x10^{-9}T^3 + 7.051x10^{-13}T^4$

These expressions should be applicable at temperatures in excess of 800 K, with an uncertainty of a factor of 3. Above 1500 K, decomposition is the predominant path. However, lifetimes of radicals at such temperatures are very short. Reaction is probably unimportant.

Table A. logk(decomp.)/k(decomp. + stab.) as a function of concentration and temperature

log[M]	T/K										
	500	700	900	1100	1300	1500	1700	1900	2100	2300	2500
16.0	-1.30	-0.63	-0.27	-0.10	-0.03	-0.01					
16.5	-1.76	-0.97	-0.46	-0.19	-0.07	-0.03	-0.01				
17.0	-2.24	-1.37	-0.73	-0.34	-0.15	-0.06	-0.02	-0.01			
17.5	-2.73	-1.82	-1.08	-0.57	-0.28	-0.13	-0.06	-0.03	-0.01	-0.01	
18.0	-3.23	-2.30	-1.48	-0.87	-0.48	-0.25	-0.13	-0.06	-0.03	-0.02	-0.01
18.5	-3.73	-2.79	-1.94	-1.24	-0.75	-0.44	-0.25	-0.14	-0.07	-0.04	-0.02
19.0	-4.23	-3.29	-2.42	-1.67	-1.11	-0.71	-0.44	-0.27	-0.16	-0.10	-0.06
19.5	-4.73	-3.79	-2.91	-2.14	-1.53	-1.06	-0.72	-0.48	-0.32	-0.21	-0.14
20.0	-5.23	-4.29	-3.41	-2.63	-1.99	-1.48	1.08	-0.78	0.56	0.40	0.29
20.5	-5.73	-4.79	-3.90	-3.12	-2.47	-1.94	-1.51	-1.17	-0.90	-0.69	-0.54
21.0	-6.23	-5.29	-4.40	-3.62	-2.97	-2.43	-1.98	-1.62	-1.32	-1.08	-0.89

Table B. Collision efficiency $\beta(e)$ as a function of downward step size and temperature

T/K	Step-size (cm^{-1})				
	150	300	600	1200	2400
500	5.17×10^{-2}	1.37×10^{-1}	2.92×10^{-1}	4.93×10^{-1}	6.80×10^{-1}
700	2.36×10^{-2}	7.09×10^{-2}	1.77×10^{-1}	3.51×10^{-1}	5.53×10^{-1}
900	1.10×10^{-2}	3.61×10^{-2}	1.02×10^{-1}	2.34×10^{-1}	4.26×10^{-1}
1100	5.04×10^{-3}	1.76×10^{-2}	5.49×10^{-2}	1.44×10^{-1}	3.03×10^{-1}
1300	2.31×10^{-3}	8.41×10^{-3}	2.82×10^{-2}	8.27×10^{-2}	2.00×10^{-1}
1500	1.14×10^{-3}	4.28×10^{-3}	1.50×10^{-2}	4.76×10^{-2}	1.28×10^{-1}
1700	6.03×10^{-4}	2.29×10^{-3}	8.28×10^{-3}	2.75×10^{-2}	7.97×10^{-2}
1900	3.13×10^{-4}	1.20×10^{-3}	4.39×10^{-3}	1.50×10^{-2}	4.54×10^{-2}
2100	1.50×10^{-4}	5.74×10^{-4}	2.11×10^{-3}	7.26×10^{-3}	2.25×10^{-2}
2300	6.39×10^{-5}	2.44×10^{-4}	8.96×10^{-4}	3.07×10^{-3}	9.53×10^{-3}
2500	2.41×10^{-5}	9.18×10^{-5}	3.35×10^{-4}	1.14×10^{-3}	3.50×10^{-3}

(W. Tsang, April 1986)

44,20 $t\text{-}C_4H_9 + C_2H_2 \rightarrow (CH_3)_3CCH{=}CH$ (a)
$\rightarrow CH_2{=}C(CH_3)CH{=}CH_2 + CH_3$ (b)

Reference	Conditions Temp./K	[M]/molecule cm^{-3}	Reaction rate constant, $k/cm^3molecule^{-1}s^{-1}$	Uncertainty factor
Recommended value			$k_b=4.6x10^{-14}exp(-3323/T)$	3

Comments and Recommendations

Although there does not appear to have been any measurements on the rate constants for this process, it must be very similar to the analogous reaction of isopropyl with acetylene (42,20). At combustion temperatures 1,4 H-transfer will occur leading to isoprene and methyl radical formation. The rate expression for the overall process is

$k_b = 4.6x10^{-14}exp(-3323/T)cm^3molecule^{-1}s^{-1}$

The uncertainty is a factor of 3.

(W. Tsang, April 1986)

44,21 $t\text{-}C_4H_9 + C_2H \rightarrow i\text{-}C_4H_8 + C_2H_2$ (a)
$\rightarrow C_6H_{10}$ (3,3-Dimethylbutyne-1) (b)
$\rightarrow C_5H_7 + CH_3$ (c)

Reference	Conditions Temp./K	[M]/molecule cm^{-3}	Reaction rate constant, $k/cm^3molecule^{-1}s^{-1}$	Uncertainty factor
Recommended value			$k_{b+c}=1.6x10^{-11}(300/T)^{0.75}$	3
Recommended value			$k_a=0.51x10^{-11}(300/T)^{0.75}$	3
Recommended value			$logk_c/k_{b+c}(N_2,1) = -6.557+ 1.382x10^{-2}T-1.082x10^{-5}T^2+ 3.698x10^{-9}T^3-4.672x10^{-13}T^4$	3

Comments and Recommendations

There are no measurements on the rate constants for these processes. We suggest the use of expressions from the reactions of ethyl+t-butyl (44,17). This leads to $k_{b+c}=1.6x10^{-11}(300/T)^{0.75}$ $cm^3molecule^{-1}s^{-1}$ and $k_a/k_{b+c} \geq 0.32$. The estimated uncertainties are factors of 3.

The pressure dependence for the decomposition process (c), as opposed to the stabilization plus decomposition can be found in Table A, on the basis of the strong collision assumption and with the reactant as the collider. Table B gives collision efficiencies on a per collision basis, as a function of step size down and temperature. For N_2 and C_6H_{10} as a collider at 0.1, 1 and 10 atms. and assuming a 500 cm^{-1} and 1000 cm^{-1} step size down, respectively, we obtain the following closed expressions:

$$logk_c/k_{b+c}(N_2,0.1) = -4.430 + 1.108x10^{-2}T - 1.006x10^{-5}T^2 + 3.925x10^{-9}T^3 - 5.573x10^{-13}T^4$$

$$logk_c/k_{b+c}(N_2,1) = -6.557 + 1.386x10^{-2}T - 1.082x10^{-5}T^2 + 3.698x10^{-9}T^3 - 4.672x10^{-13}T^4$$

$$logk_c/k_{b+c}(N_2,10) = -6.617 + 9.225x10^{-3}T - 3.716x10^{-6}T^2 + 1.536x10^{-10}T^3 + 1.127x10^{-13}T^4$$

and

$$\log k_c/k_{b+c}(C_6H_{10},0.1) = -5.000 + 1.172\times10^{-2}T - 1.009\times10^{-5}T^2 + 3.772\times10^{-9}T^3 - 5.172\times10^{-13}T^4$$

$$\log k_c/k_{b+c}(C_6H_{10},1) = -6.235 + 1.123\times10^{-2}T - 7.313\times10^{-6}T^2 + 2.026\times10^{-9}T^3 - 1.993\times10^{-13}T^4$$

$$\log k_c/k_{b+c}(C_6H_{10},10) = -5.812 + 5.248\times10^{-3}T + 6.978\times10^{-7}T^2 - 1.690\times10^{-9}T^3 + 3.776\times10^{-13}T^4$$

These ratios are valid above 800 K, with an uncertainty factor of 3. Above 1500 K decomposition is the only process.

Table A. logk(decomp.)/k(decomp. + stab.) as a function of concentration and temperature

log[M]	T/K										
	500	700	900	1100	1300	1500	1700	1900	2100	2300	2500
16.0	-0.13	-0.05	-0.02	-0.01							
16.5	-0.31	-0.13	-0.06	-0.02	-0.01						
17.0	-0.59	-0.30	-0.14	-0.06	-0.03	-0.01	-0.01				
17.5	-0.98	-0.57	-0.31	-0.15	-0.07	-0.03	-0.02	-0.01			
18.0	-1.43	-0.94	-0.57	-0.31	-0.16	-0.08	-0.04	-0.02	-0.01	-0.01	
18.5	-1.91	-1.37	-0.91	-0.56	-0.32	-0.18	-0.10	-0.06	-0.03	-0.02	-0.01
19.0	-2.40	-1.85	-1.34	-0.90	-0.58	-0.36	-0.22	-0.14	-0.08	-0.05	-0.03
19.5	-2.90	-2.34	-1.80	-1.32	-0.92	-0.63	-0.43	-0.29	-0.19	-0.13	-0.09
20.0	-3.40	-2.83	-2.29	-1.78	-1.34	-0.99	-0.73	-0.53	-0.38	-0.28	-0.20
20.5	-3.90	-3.33	-2.79	-2.26	-1.81	-1.43	-1.12	-0.87	-0.68	-0.53	-0.41
21.0	-4.40	-3.83	-3.29	-2.76	-2.29	-1.90	-1.57	-1.29	-1.07	-0.88	-0.73

Table B. Collision efficiency $\beta(e)$ as a function of downward step size and temperature

T/K	Step-size (cm^{-1})				
	150	300	600	1200	2400
500	5.73×10^{-2}	1.49×10^{-1}	3.10×10^{-1}	5.12×10^{-1}	6.96×10^{-1}
700	2.83×10^{-2}	8.30×10^{-2}	2.00×10^{-1}	3.82×10^{-1}	5.84×10^{-1}
900	1.47×10^{-2}	4.69×10^{-2}	1.27×10^{-1}	2.76×10^{-1}	4.74×10^{-1}
1100	7.82×10^{-3}	2.64×10^{-2}	7.82×10^{-2}	1.91×10^{-1}	3.70×10^{-1}
1300	4.13×10^{-3}	1.46×10^{-2}	4.65×10^{-2}	1.26×10^{-1}	2.74×10^{-1}
1500	2.18×10^{-3}	7.96×10^{-3}	2.68×10^{-2}	7.93×10^{-2}	1.93×10^{-1}
1700	1.21×10^{-3}	4.50×10^{-3}	1.58×10^{-2}	4.99×10^{-2}	1.33×10^{-1}
1900	7.09×10^{-4}	2.69×10^{-3}	9.70×10^{-3}	3.20×10^{-2}	9.18×10^{-2}
2100	4.31×10^{-4}	1.65×10^{-3}	6.05×10^{-3}	2.06×10^{-2}	6.21×10^{-2}
2300	2.60×10^{-4}	1.00×10^{-3}	3.71×10^{-3}	1.29×10^{-2}	4.00×10^{-2}
2500	1.51×10^{-4}	5.81×10^{-4}	2.16×10^{-3}	7.57×10^{-3}	2.40×10^{-2}

(W. Tsang, May 1985)

44,22 $t\text{-}C_4H_9 + CH_3CO \rightarrow t\text{-}C_4H_9COCH_3$

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, $k/cm^3molecule^{-1}s^{-1}$	Uncertainty factor
Recommended value			$1.8x10^{-11}(300/T)^{0.75}$	2

Comments and Recommendations

Although there are no measurements on the rate constants for this reaction, the geometric mean rule must hold. Thus the combination rate will be $1.8x10^{-11}(300/T)^{0.75}cm^3molecule^{-1}s^{-1}$, with an uncertainty of a factor of 2.

(W. Tsang, April 1986)

44,23 $t\text{-}C_4H_9 + CH_3O_2 \rightarrow CH_3O + CH_3COCH_3 + CH_3$

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

Comments and Recommendations

Although there are no measurements on the rate constants for this reaction, the mechanism under combustion conditions is combination followed by rapid decomposition. The recommended rate constant is $2x10^{-11}cm^3molecule^{-1}s^{-1}$ with an uncertainty of a factor of 3.

(W. Tsang, April 1986)

44,24 $t\text{-}C_4H_9 + CH_3O \rightarrow i\text{-}C_4H_{10} + CH_2O$ (a)
$\rightarrow t\text{-}C_4H_9OCH_3$ (b)

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, $k/cm^3molecule^{-1}s^{-1}$	Uncertainty factor
Batt, McCulloch (1976)	363-413	$1.8x10^{19}$ i C_4H_{10}, with traces of dimethyl peroxide. Pyrolysis in static system.	k_b=$1.5x10^{-11}$	3
Recommended value			k_a=$1.6x10^{-11}$	5
Recommended value			k_b=$1.5x10^{-11}$	3

Comments and Recommendations

The result of Batt and McCulloch is derived from the geometric mean rule. We have adjusted their rate constants to reflect our recommendations for the combination of t-butyl (44,44). We recommend $k_b = 1.5x10^{-11}cm^3molecule^{-1}s^{-1}$, with an uncertainty of a factor of 3. For the disproportionation reaction we recommend

$$k_a = 1.6\times10^{-11}\mathrm{cm^3molecule^{-1}s^{-1}},$$

with an uncertainty at a factor of 5.

(W. Tsang, April 1986)

References

Batt, L., and McCulloch, R. D., "Pyrolysis of Dimethyl Peroxide," Int. J. Chem. Kinet. 8, 491 (1976)

44,25 $t\text{-}C_4H_9 + {}^1CH_2 \rightarrow i\text{-}C_4H_8 + CH_3$

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

Comments and Recommendations

Although there are no measurements on the rate constants for this reaction, the measurements for ${}^1CH_2$ with methane (25,10) and ethane (25,11) have now resolved the problem posed by the non-selective nature of methylene insertion and the low rate constants recommended by Laufer (Rev. Chem. Int. 4, 225 (1981)). We recommend $3\times10^{-10}\mathrm{cm^3molecule^{-1}s^{-1}}$ with an uncertainty of a factor of 2.

(W. Tsang, May 1986)

44,26 $t\text{-}C_4H_9 + {}^3CH_2 \rightarrow i\text{-}C_4H_8 + CH_3$

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, $k/cm^3molecule^{-1}s^{-1}$	Uncertainty factor
Recommended value			$2.7\times10^{-11}(300/T)$	2

Comments and Recommendations

Although there are no measurements on the rate constants for this process, there is little question that the mechanism involves combination with a rate constant similar to that for t-butyl + methyl (44,16), followed by decomposition of the hot adduct. The recommended rate expression is $2.7\times10^{-11}(300/T)\mathrm{cm^3molecule^{-1}s^{-1}}$, with an uncertainty of a factor of 2.

(W. Tsang, April 1986)

44,38 $t\text{-}C_4H_9 + CH_3OH \rightarrow i\text{-}C_4H_{10} + CH_2OH$ (a)
$\rightarrow t\text{-}C_4H_{10} + CH_3O$ (b)

	Conditions		Reaction rate constant,	Uncertainty
Reference	Temp./K	[M]/molecule cm^{-3}	k/cm^{3}molecule^{-1}s^{-1}	factor
log K_p(a) = 0.986 - 1.24x10^3/T + 4.65X10^5/T^2 - 5.41x10^7/T^3				
log K_p(b) = -0.575 - 3.06x10^3/T + 5.145x10^5/T^2 - 6.457x10^7/T^3				
Recommended value			k_a=1.3x10^{-28}T$^{4.7}$exp(-4572/T)	10
Recommended value			k_b=2.5x10^{-21}T$^{1.8}$exp(-4709/T)	10

Comments and Recommendations

There are no measurements on the rate constants for these reactions. From our estimate for hydroxymethyl attack on isobutane (43,39) and detailed balance we recommend

k_a = 1.3x10^{-28}T$^{4.7}$exp(-4572/T)cm^{3}molecule^{-1}s^{-1}

In a similar manner, for the formation of methoxy we use our recommendation for the reverse reaction (43,24) and the equilibrium constant and obtain

k_b = 2.5x10^{-21}T$^{1.8}$exp(-4709/T)cm^{3}molecule^{-1}s^{-1}

The uncertainty is an order of magnitude.

(W. Tsang, April 1986)

44,39 $t\text{-}C_4H_9 + CH_2OH \rightarrow i\text{-}C_4H_{10} + HCHO$ (a)
$\rightarrow C_4H_8 + CH_3OH$ (b)
$\rightarrow C_5H_{11}OH$ (c)

	Conditions		Reaction rate constant,	Uncertainty
Reference	Temp./K	[M]/molecule cm^{-3}	k/cm^{3}molecule^{-1}s^{-1}	factor
Recommended value			k_c=1.6x10 ^{11}(300/T)$^{0.75}$	2
Recommended value			k_a=0.8x10^{-11}(300/T)$^{0.75}$	3
Recommended value			k_b=0.5x10^{-11}(300/T)$^{0.75}$	3

Comments and Recommendations

There are no measurements on the rate constants for these reactions. We suggest the use of the rate expression for $t\text{-}C_4H_9 + C_2H_5$ (44,17). This leads to k_c = 1.6x10^{-11}(300/T)$^{0.75}$cm^{3}molecule^{-1}s^{-1}, with an uncertainty of a factor of 2, and k_a/k_c = 0.52, k_b/k_c = 0.32, with uncertainties of factors of 3 for the disproportionation reactions.

(W. Tsang, April 1986)

44,40 $t\text{-}C_4H_9 + C_3H_8 \rightarrow i\text{-}C_4H_{10} + n\text{-}C_3H_7$ **(a)**
$\rightarrow i\text{-}C_4H_{10} + i\text{-}C_3H_7$ **(b)**

	Conditions			
Reference	Temp./K	[M]/molecule cm^{-3}	Reaction rate constant, k/cm^{3}molecule^{-1}s^{-1}	Uncertainty factor
$\log K_p(a) = 0.987 - 2.21\times10^3/T + 4.525\times10^5/T^2 - 5.73\times10^7/T^3$				
$\log K_p(b) = 0.595 - 1.45\times10^3/T + 3.355\times10^5/T^2 - 4.52\times10^7/T^3$				
Recommended value			$k_a=1.9\times10^{-29}T^{5.0}\exp(-4808/T)$	6
Recommended value			$k_b=1.8\times10^{-30}T^{5.16}\exp(-4091/T)$	6

Comments and Recommendations

Although there are no measurements on the rate constants for these reactions, on the basis of our estimates for the reverse reactions (43,41) and (43,42) and the equilibrium constants, we recommend

$k_a=1.9\times10^{-29}T^{5.0}\exp(-4808/T)\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$ and
$kb=1.8\times10^{-30}T^{5.16}\exp(-4091/T)\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$.

We estimate the uncertainty to be a factor of 6.

(W. Tsang, April 1986)

44,41 $t\text{-}C_4H_9 + n\text{-}C_3H_7 \rightarrow i\text{-}C_4H_{10} + C_3H_6$ **(a)**
$\rightarrow i\text{-}C_4H_8 + C_3H_8$ **(b)**
$\rightarrow CH_3C(CH_3)_2CH_2CH_2CH_3$ **(c)**

	Conditions			
Reference	Temp./K	[M]/molecule cm^{-3}	Reaction rate constant, k/cm^{3}molecule^{-1}s^{-1}	Uncertainty factor
Recommended value			$k_c=1.6\times10^{-11}(300/T)^{0.75}$	1.5
Recommended value			$k_a=0.5\times10^{-11}(300/T)^{0.75}$	2
Recommended value			$k_b=0.8\times10^{-11}(300/T)^{0.75}$	2

Comments and Recommendations

There are no rate measurements for these reactions. From the geometric mean rule k_c has been found to be $k_c=1.6\times10^{-11}(300/T)^{0.75}$, with an uncertainty of a factor of 1.5. From analogous processes, $k_a/k_c = 0.3\pm0.2$ and $k_b/k_c = 0.5\pm0.1$.

(W. Tsang, April 1986)

44,42 $t\text{-}C_4H_9 + i\text{-}C_3H_7 \rightarrow i\text{-}C_4H_{10} + C_3H_6$ (a)

$\rightarrow i\text{-}C_4H_8 + C_3H_8$ (b)

$\rightarrow CH_3C(CH_3)_2CH(CH_3)_2$ (c)

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, $k/cm^3molecule^{-1}s^{-1}$	Uncertainty factor
Gibian, Corley (1973) review			k_a/k_c=0.67 k_b/k_c=0.7	1.1 1.1
Recommended value			k_c=1.3x10^{-11}(300/T)$^{1.1}$	1.5
Recommended value			k_a=0.9x10^{-11}(300/T)$^{1.1}$	1.7
Recommended value			k_b=0.9x10^{-11}(300/T)$^{1.1}$	1.7

Comments and Recommendations

The disproportionation to combination ratio for these reactions should not have an error greater than 15%. The combination rate constant can be determined from the geometric mean rule and is

k_c=1.3x10^{-11}(300/T)$^{1.1}$cm^{3}molecule^{-1}s^{-1},

with an uncertainty of a factor of 1.5

(W. Tsang, April 1986)

44,43 $t\text{-}C_4H_9 + i\text{-}C_4H_{10} \rightarrow i\text{-}C_4H_{10} + i\text{-}C_4H_9$

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, $k/cm^3molecule^{-1}s^{-1}$	Uncertainty factor
Recommended value			8.4x10^{-30}T$^{5.17}$exp(-4563/T)	4

Comments and Recommendations

Although there are no measurements on the rate constant for this process, they should parallel the value for $t\text{-}C_4H_9$+C_2H_6 (44,11). Thus we recommend

8.4x10^{-30}T$^{5.17}$exp(-4563/T)cm^{3}molecule^{-1}s^{-1}

The estimated uncertainty is a factor of 4.

(W. Tsang, October 1987)

44,44 $2t\text{-}C_4H_9 \rightarrow C_8H_{18}$ (a)

$\rightarrow C_4H_8 + C_4H_{10}$ (b)

	Conditions		Reaction rate constant,	Uncertainty
Reference	Temp./K	[M]/molecule cm^{-3}	$k/cm^3molecule^{-1}s^{-1}$	factor
Anastasi, Arthur (1987)	308	$2.2x10^{18}$ N_2 $0.4x10^{18}$ azoisobutane photolysis with molecular modulation spectroscopy	k_a=$2.6x10^{-12}$ k_b/k_a=2.3	1.3 1.3
Arthur (1986)	300-421	$(0.2-1.6)x10^{19}$ N_2 with traces of azoisobutane	k_a=$2.7x10^{-12}(300/T)^{1.73}$ k_a/k_b=2.3	1.3
Bethune, et al. (1981)		~ $2x10^{17}$ 2-methyl-2-nitroso propane; flash photolysis, ir detection	k_a=$7.5x10^{-12}$ k_b/k_a=2.9	2
Choo, et al. (1976)	700	very low pressure pyrolysis of azoisobutane 2-methyl-2-nitroso propane	$1.1x10^{-12}$ k_b/k_a=2.8	2
Parkes, Quinn (1976)	250-450	$2x10^{19}$ N_2 0.5-1% azoisobutane modulation spectroscopy	k_a=$(4\pm0.6)(300/T)^{1.5}x10^{-12}$	1.3
Gibian, Corley (1973) review			k_b/k_a=2.7	1.1
Recommended value			k_a=$4x10^{-12}(300/T)^{1.5}$)	1.5 at 300K, 2 at 1000K
Recommended value			k_a/k_b=2.7	1.1

Comments and Recommendations

For the combination reaction we recommend the rate expression of Parkes and Quinn with an uncertainty of 50% near room temperature and increasing to a factor of 2 at 1000 K. The disproportionation to combination ratio given in Gibian and Corley is based on many studies at room temperature and is accurate to 10%. The slower rate, compared to other alkyl radicals, and the negative temperature dependence seem to be well established.

Figure 6 contains Arrhenius plots of the experimental values of rate constants for the combination reactions of t-butyl radicals and our recommended values.

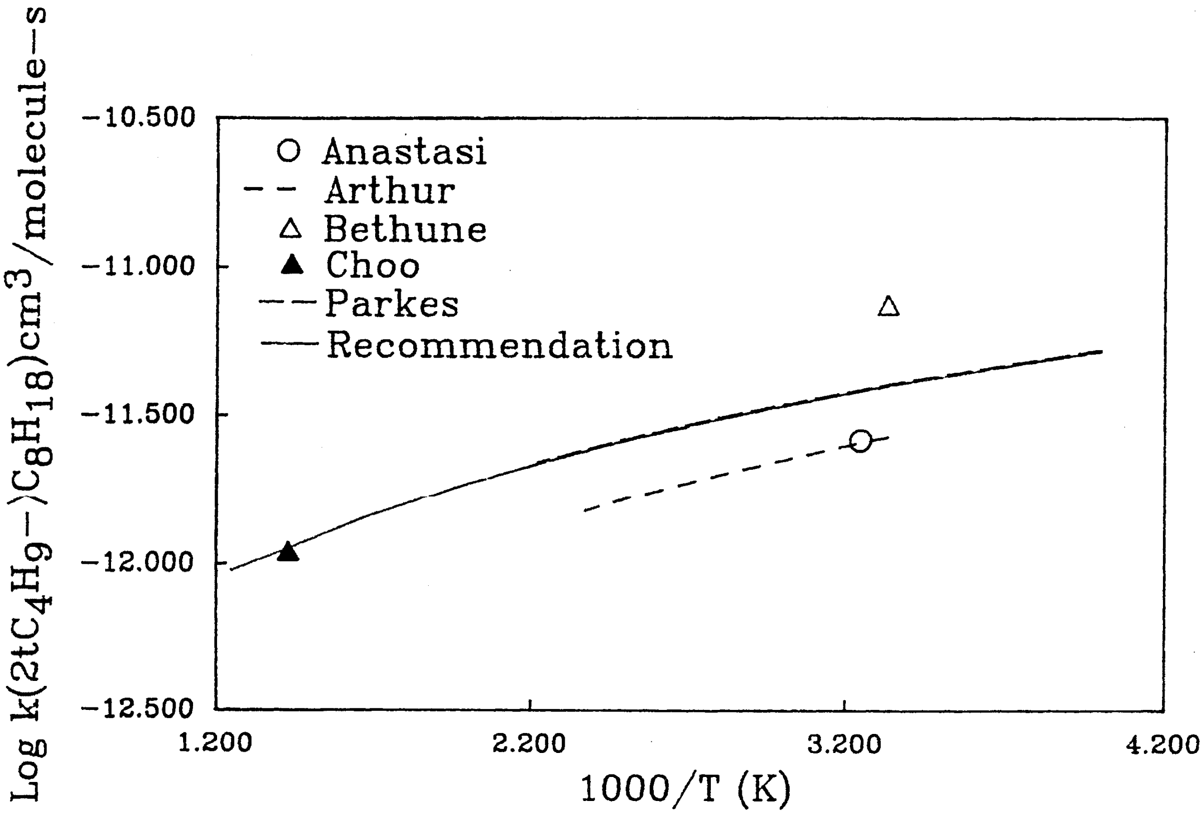

Fig. 6. Previous results and current recommendations on the combination rate constants for t-Butyl radicals (W. Tsang, April 1986)

References

Anastasi, C., and Arthur, N. L., "Rate Constants for the Reactions of CH_3 Radicals with C_2H_5, i-C_3H_7 and t-C_4H_9 Radicals," J. Chem. Soc., Faraday Trans. 2 83, 277 (1987).

Arthur, N. L., "Absorption Cross Sections and Mutual Rate Constants for C_2H_5 and t-C_4H_9 Reactions," J. Chem. Soc., Faraday Trans. 2 83, 1057 (1986).

Bethune, D. S., Lankard, J. R., Sorokin, P. P., Schell-Sorokin, A. J., Plecenik, R. M., and Avouris, Ph., "Time-Resolved Infrared Study of Bimolecular Reactions between tert-butyl Radicals," J. Chem. Phys. 75, 2231 (1981)

Choo, K. Y., Beadle, P. C., Piszkiewicz, L. W., and Golden, D. M.,"An Absolute Measurement of the Rate Constant for t-Butyl Radical Combination," Int. J. Chem. Kinet. 8, 45 (1976)

Gibian, M. J., and Corley, R. C., "Organic Radical-Radical Reactions. Disproportionation vs Combination," Chem. Rev. 73, 443 (1973)

45,1 $i\text{-}C_4H_9 \rightarrow C_3H_6 + CH_3$

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, $k/cm^3molecule^{-1}s^{-1}$	Uncertainty factor
Metcalfe, Trotman Dickenson (1960)	550-690	$6x10^{17}$ isovaleraldehyde photolysis	$2x10^{12}exp(-13190/T)s^{-1}$	
Slater et al. (1968)	543-598	10^{17} azoisobutane photolysis	$1.6x10^{12}exp(-15600/T)s^{-1}$	
Recommended value	300-1500		$2x10^{13}exp(-15075/T)s^{-1}$ $logk/k_\infty(N_2,1.0)=-0.120$ $+1.118x10^{-3}T-1.776x10^{-6}T^2$ $+3.911x10^{-10}T^3$	4

Comments and Recommendations

The rate expressions given above have been adjusted so as to be consistent with our combination rate constants for isobutyl radicals (45,45). Nevertheless, the rate constants are widely discordant; the actual difference being a factor of 55 at 600 K, even after taking into account that the results of Slater et al are slightly into the falloff region. Furthermore from the data of Miyoshi and Brinton (J. Phys. Chem. 36, 309 (1962)), the rate constant for methyl addition onto the nonterminal carbon is estimated to be approximately 10% of the terminal addition. Combination of this data with our thermodynamics for the isobutyl radical leads to a rate constant of $2.66x10^{-4}s^{-1}$. With an A-factor of $2x10^{13}s^{-1}$ or twice that for n-propyl radical decomposition this leads to the rate expression $k_{45,1}) = 2x10^{13}exp(-15549/T)s^{-1}$, leading to a rate constant at 600 K of $111s^{-1}$. The results of Metcalfe and Trotman-Dickenson give $567s^{-1}$ (600K) while those of Slater and Calvert yield $8.2s^{-1}$ (600K).

The experimental procedure used by Metcalfe and Trotman-Dickenson has been successfully used to determine the rate constants for n-propyl (41,41), isopropyl (42,42) and t-butyl radical (44,44) decomposition. In the present case the adoption of their measurements will lead to the conclusion that the main reaction for methyl addition to propylene will be at the nonterminal position. This cannot be correct. On the other hand the results of Slater and Calvert lead to the conclusion that methyl substitution leads to a strengthening of the beta C-C bond in alkyl radicals. This is not the case for beta carbon hydrogen bonds. It also leads to the conclusion that non-terminal methyl addition is less than 1% of the terminal addition. Furthermore, the methodology used by Slater and Calvert leads to an unacceptably low value for isobutyl radical attack on O_2 (see 45,3).

We recommend a rate expression that yields rate constants that are intermediate between the measurements of Metcalfe and Trotman-Dickenson and our calculated numbers and with an A-factor of $2x10^{13}s^{-1}$. The rate expression is thus

$$k_{45,1} = 2x10^{13}exp(-15070/T)s^{-1}$$

Figure 7 contains a plot of the data and our recommendations. RRKM calculations for the fall-off effects can be found in Table A assuming strong collisions. Weak collisional effects are summarized in Table B.

For N_2 and isobutane as the third bodies the temperature dependence of k/k_∞ at 0.1,1 and 10 atms and with step size down of $500cm^{-1}$ can be expressed, respectively, by the following relations:

$logk/k_\infty(N_2,0.1) = -1.197 + 5.998x10^{-3}T - 9.062x10^{-6}T^2 + 4.060x10^{-9}T^3 - 6.132x10^{-13}T^4$

$logk/k_\infty(N_2,1.0) = -0.120 + 1.118x10^{-3}T - 1.776x10^{-6}T^2 + 3.911x10^{-10}T^3$

$\log k/k_{\infty}(N_2,10) = -0.317 + 1.205\times10^{-3}T - 1.236\times10^{-6}T^2 + 2.327\times10^{-10}T^3$

$\log k/k_{\infty}(i\text{-}C_4H_9,0.1) = -1.158 + 5.209\times10^{-3}T - 7.184\times10^{-6}T^2 + 3.047\times10^{-9}T^3 - 4.438\times10^{-13}T^4$
$\log k/k_{\infty}(i\text{-}C_4H_9,1.0) = -0.277 + 1.251\times10^{-3}T - 1.471\times10^{-6}T^2 + 2.929\times10^{-10}T^3$
$\log k/k_{\infty}i\text{-}C_4H_9,10) = -0.223 + 7.463\times10^{-4}T - 6.695\times10^{-7}T^2 + 1.042\times10^{-10}T^3$

Due to the number of inconsistencies mentioned above we assign an uncertainty of a factor of 4. Some new measurements to check the issues raised here would be helpful. Note that our recommendations are for the temperature range 300-1500 K. The calculated weak collider effects in the RRKM formulation we use becomes increasingly unreliable at higher temperatures.

Table A. $\log(k/k_{\infty})$ for the unimolecular decomposition of isobutyl radicals as function of temperature and pressure assuming strong collisions

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				-0.01	-0.02	-0.04	-0.06	-0.10	-0.14	-0.19	-0.25
20.5					-0.01	-0.00	-0.01	-0.01	-0.02	-0.03	-0.04
21.0							-0.01	-0.01	-0.02	-0.03	-0.04

Table B. Collision efficiency $\beta(c)$ as a function of downward step size and temperature

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	6.28×10^{-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}	1.45×10^{-1}	3.41×10^{-1}
1300	4.12×10^{-3}	1.51×10^{-2}	5.17×10^{-2}	1.57×10^{-1}	4.06×10^{-1}
1500	4.83×10^{-3}	1.78×10^{-2}	6.16×10^{-2}	1.92×10^{-1}	5.23×10^{-1}
1700	5.97×10^{-3}	2.20×10^{-2}	7.59×10^{-2}	2.38×10^{-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	9.88×10^{-3}	3.59×10^{-2}	1.21×10^{-1}	3.70×10^{-1}	$1.00\times10^{+0}$
2500	1.10×10^{-2}	3.99×10^{-2}	1.34×10^{-1}	4.06×10^{-1}	$1.09\times10^{+0}$

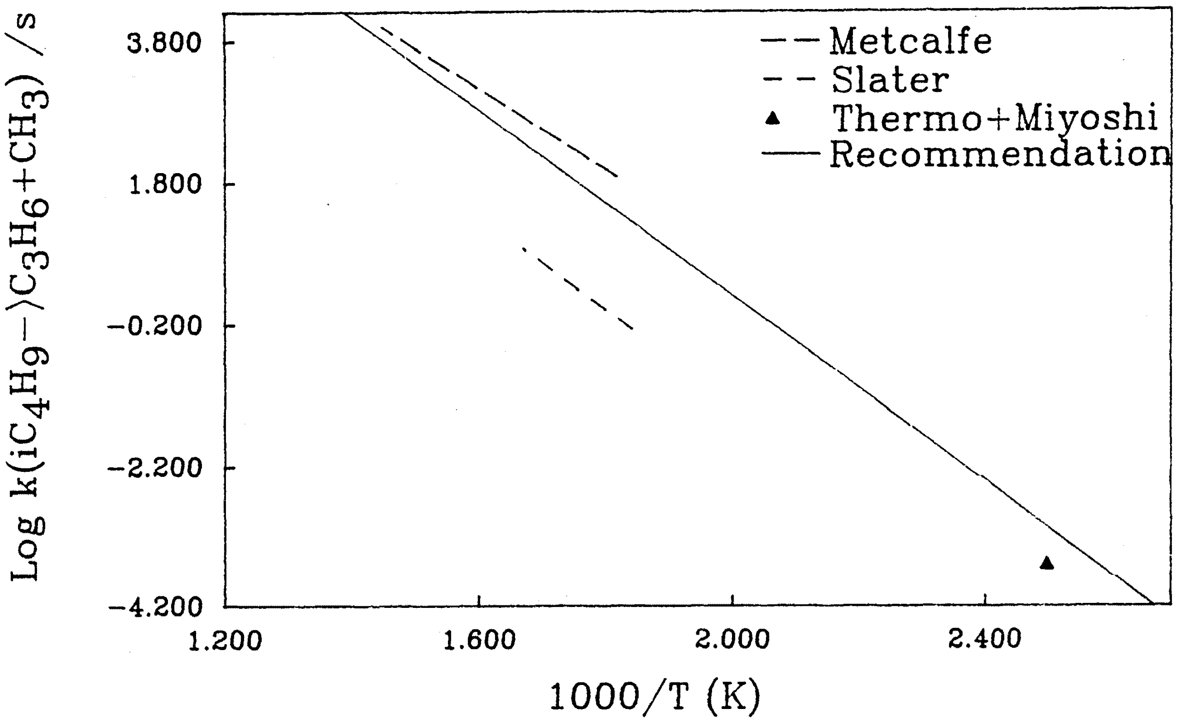

Fig. 7. Plots of the experimental data and current recommendations for reaction 45,1.

(W. Tsang, June 1987)

References

Metcalfe, E. L., and Trotman-Dickenson, A. F., "The Reactions of Alkyl Radicals from the Photolysis of Isovaleraldehyde," J. Chem. Soc., 5072 (1960)

Slater, D. H., Collier, S. S., and Calvert, J., "The Photolysis of 1,1'-Azoisobutane Vapor at 3660A. The Reactions of Isobutyl Free Radical", J. Amer. Chem. Soc. **90**, 268 (1968)

Miyoshi, M., and Brinton, R. K., "Gaseous Reaction of Methyl Radicals with Propylene," J. Chem. Phys. **36**, 3019 (1962)

45,2 $i\text{-}C_4H_9 + H_2 \rightarrow i\text{-}C_4H_{10} + H$

	Conditions		Reaction rate constant,	Uncertainty
Reference	Temp./K	[M]/molecule cm^{-3}	$k/cm^3 molecule^{-1} s^{-1}$	factor
$\log K_p = 2.091 - 931.5/T + 1.134\times10^5/T^2 - 1.738\times10^7/T^3$				
Recommended value			$4.7\times10^{-21} T^{2.72} \exp(-4930/T)$	3

Comments and Recommendations

There are no data. We recommend the rate expression:

$k_{45,2} = 4.7\text{x}10^{-21}T^{2.72}\exp(-4930/T)\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$

This is based on the recommended rate expression for the reverse reaction (43,4) and is in substantial agreement with our expressions for n-propyl and ethyl attack on H_2. The uncertainty is a factor of 3.

(W. Tsang, June 1987)

45,3 $i\text{-}C_4H_9 + O_2 \rightarrow i\text{-}C_4H_8 + HO_2$ (a)

$\rightarrow i\text{-}C_4H_9O_2$ (b)

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, k/cm^{3}molecule^{-1}s^{-1}	Uncertainty factor
Baker et al. (1979)	753	6.5-65x10^{15} $i\text{-}C_4H_{10}$ 1.8-5.4x10^{18} H_2, 0.9x10^{18} O_2 N_2 to 6.5x10^{18} total pressure static system and g.c. analysis of all products	$k_{45,3}/k_{45,1}=1.29\text{x}10^{-18}$	1.5
Slater, Calvert (1968)	308-405	7.8-20.1x10^{16} Azoisobutane 0-2.6x10^{17} O_2 photolysis and g.c. analysis	$k_{a+b}=4.3\text{x}10^{-15}$ $k_a(311)=4.3\text{x}10^{-16}$	3
Recommended values	600-1000		$k_a=4\text{x}10^{-14}$	5
	<600		$k_b=2.7\text{x}10^{-5}/T^{2.7}$	3

Comments and Recommendations

For channel (a), we recommend the experimental results of Baker et al. In combination with our recommendation for the rate expression for isobutyl radical decomposiition this leads to a rate constant at 753 K of $4\text{x}10^{-14}\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$. This is a factor of 3 lower than the recommendation of Baker et al, which is based of the rate constant measurements of Metcalfe and Trotman-Dickenson (J. Chem. Soc., 5072 (1960)) for isobutyl radical decomposition. Note our comments in 45,1. With an uncertainty of a factor of 5, the rate constant of $4\text{x}10^{-14}\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$ is applicable over the temperature range of 600-1000 K.

On the basis of our recommendations for n-propyl radicals, below 500K the main reaction is addition and the rate expression on the basis of the results of Slagle et al. (Symp. Combust. **20**, (Combustion Institute, Pittsburgh, (1984) 733) is $k_b=2.7\text{x}10^{-5}/T^{2.7}\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$ and the estimated uncertainty is a factor of 3. Note that Slagle et al. have presented strong evidence for the coupling of channels a and b through the hot adduct from reaction a. The actual pressure and temperature dependences may be far more complex than that presented here. Above 1000 K the instability of isobutyl radical makes these reactions unlikely to be of any importance under combustion conditions.

We have not factored into our analysis the results of Slater and Calvert. Their rate constant for the sum of channels a and b is unacceptably small.
(W. Tsang, November 1987)

References

Baker, R. R., Baldwin, R. R., and Walker, R.W., "Addition of i-Butane to Slowly Reacting Mixtures of Hydrogen and Oxygen at 480C," J. Chem. Soc. Faraday I 74, 2229 (1978).

Slater, D. H., and Calvert, J. G., "The Photooxidation of 1,1'-Azoisobutane," Adv. Chem. Ser. **76**, 58 (1968).

45,4 $i\text{-}C_4H_9 + H \rightarrow C_4H_{10}$ (a)
$\rightarrow i\text{-}C_3H_7 + CH_3$ (b)
$\rightarrow i\text{-}C_4H_8 + H_2$ (c)

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, k/cm^{3}molecule^{-1}s^{-1}	Uncertainty factor
Recommended value			$k_{a+b}=6\times10^{-11}$	1.5
Recommended value			$k_c=1.5\times10^{-12}$	2
Recommended value			$\log k_b/k_{b+c}(N_2,1.0)=-8.253+1.343\times10^{-2}T-7.232\times10^{-6}T^2+1.344\times10^{-9}T^3-2.777\times10^{-14}T^4$	

Comments and Recommendations

There are no data. However the mechanism is clear. Addition (a) which will lead to a hot adduct which can be stabilized or decompose through C-C bond scission (b) and disproportionation to form the olefin and H_2 (c). We recommend the rate expressions

$k_{a+b} = 6\times10^{-11}\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$
$k_c = 1.5\times10^{-12}\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$

with uncertainties of a factor of 1.5 and 2 respectively. These are the expressions we recommended for H + n-propyl, except that for the latter we have decreased the rate constant by a factor of two in order to account for the one hydrogen atom that is available. Due to the presence of the decomposition channel k_{a+b} is not pressure dependent. The branching ratio has however some pressure dependence. The results of RRKM calculation on a strong collision basis can be found in Table A. Weak collision effects can be found in Table B.

Table A. log(k_b/k_{b+c}), decomposition to decomposition plus stabilization, for H+isobutyl radical combination as a function of temperature and pressure assuming strong collisions

log[M]	T/K											
	300	500	700	900	1100	1300	1500	1700	1900	2100	2300	2500
16.0	-1.89	-1.02	-0.44	-0.17	-0.06	-0.02	-0.01					
16.5	-2.38	-1.42	-0.69	-0.30	-0.12	-0.05	-0.02	-0.01				
17.0	-2.88	-1.88	-1.02	-0.49	-0.23	-0.10	-0.04	-0.02	-0.01			
17.5	-3.38	-2.36	-1.41	-0.76	-0.39	-0.19	-0.09	-0.04	-0.02	-0.01		
18.0	-3.88	-2.85	-1.85	-1.10	-0.62	-0.34	-0.18	-0.09	-0.05	-0.02	-0.01	-0.01
18.5	-4.38	-3.35	-2.32	-1.50	-0.93	-0.56	-0.32	-0.18	-0.10	-0.05	-0.03	-0.02
19.0	-4.88	-3.85	-2.81	-1.95	-1.31	-0.85	-0.53	-0.32	-0.20	-0.12	-0.07	-0.04
19.5	-5.38	-4.35	-3.31	-2.43	-1.74	-1.21	-0.82	-0.54	-0.35	-0.23	-0.15	-0.10
20.0	-5.88	-4.85	-3.80	-2.92	-2.21	-1.63	-1.18	-0.84	-0.59	-0.41	-0.29	-0.21
20.5	-6.38	-5.35	-4.30	-3.42	-2.69	-2.09	-1.60	-1.21	-0.91	-0.68	-0.52	-0.40
21.0	-6.88	-5.85	-4.80	-3.92	-3.19	-2.58	-2.07	-1.65	-1.31	-1.04	-0.83	-0.68

Table B. Collision efficiency β_c as a function of downward step size and temperature

T/K	Step-size (cm^{-1})				
	150	300	600	1200	2400
300	$1.34\text{x}10^{-1}$	$2.87\text{x}10^{-1}$	$4.86\text{x}10^{-1}$	$6.75\text{x}10^{-1}$	$8.14\text{x}10^{-1}$
500	$5.97\text{x}10^{-2}$	$1.54\text{x}10^{-1}$	$3.18\text{x}10^{-1}$	$5.20\text{x}10^{-1}$	$7.02\text{x}10^{-1}$
700	$2.99\text{x}10^{-2}$	$8.70\text{x}10^{-2}$	$2.08\text{x}10^{-1}$	$3.92\text{x}10^{-1}$	$5.93\text{x}10^{-1}$
900	$1.59\text{x}10^{-2}$	$5.03\text{x}10^{-2}$	$1.34\text{x}10^{-1}$	$2.88\text{x}10^{-1}$	$4.87\text{x}10^{-1}$
1100	$8.73\text{x}10^{-3}$	$2.92\text{x}10^{-2}$	$8.52\text{x}10^{-2}$	$2.04\text{x}10^{-1}$	$3.87\text{x}10^{-1}$
1300	$4.80\text{x}10^{-3}$	$1.68\text{x}10^{-2}$	$5.27\text{x}10^{-2}$	$1.39\text{x}10^{-1}$	$2.96\text{x}10^{-1}$
1500	$2.66\text{x}10^{-3}$	$9.61\text{x}10^{-3}$	$3.19\text{x}10^{-2}$	$9.18\text{x}10^{-2}$	$2.16\text{x}10^{-1}$
1700	$1.52\text{x}10^{-3}$	$5.65\text{x}10^{-3}$	$1.95\text{x}10^{-2}$	$6.02\text{x}10^{-2}$	$1.55\text{x}10^{-1}$
1900	$9.28\text{x}10^{-4}$	$3.49\text{x}10^{-3}$	$1.24\text{x}10^{-2}$	$4.02\text{x}10^{-2}$	$1.11\text{x}10^{-1}$
2100	$5.90\text{x}10^{-4}$	$2.24\text{x}10^{-3}$	$8.15\text{x}10^{-3}$	$2.73\text{x}10^{-2}$	$7.96\text{x}10^{-2}$
2300	$3.81\text{x}10^{-4}$	$1.46\text{x}10^{-3}$	$5.36\text{x}10^{-3}$	$1.83\text{x}10^{-2}$	$5.57\text{x}10^{-2}$
2500	$2.43\text{x}10^{-4}$	$9.34\text{x}10^{-4}$	$3.46\text{x}10^{-3}$	$1.20\text{x}10^{-2}$	$3.74\text{x}10^{-2}$

For N_2 and isobutane as third bodies the temperature dependence of k_b/k_{b+c} at 0.1, 1 and 10 atmospheres can be expressed by the following relations:

$\log k_b/k_{b+c}(N_2,0.1) = -7.708 + 1.637\text{x}10^{-2}T - 1.270\text{x}10^{-5}T^2 + 4.275\text{x}10^{-9}T^3 - 5.281\text{x}10^{-13}T^4$

$\log k_b/k_{b+c}(N_2,1.0) = -8.253 + 1.343\text{x}10^{-2}T - 7.232\text{x}10^{-6}T^2 + 1.344\text{x}10^{-9}T^3 - 2.777\text{x}10^{-14}T^4$

$\log k_b/k_{b+c}(N_2,10) = -8.558 + 9.757\text{x}10^{-3}T - 1.696\text{x}10^{-6}T^2 - 1.282\text{x}10^{-9}T^3 + 3.797\text{x}10^{-13}T^4$

$\log k_{b+c}(i\text{-}C_4H_{10},0.1) = -7.663 + 1.442\text{x}10^{-2}T - 9.729\text{x}10^{-6}T^2 + 2.772\text{x}10^{-9}T^3 - 2.782\text{x}10^{-13}T^4$

$\log k_{b+c}(i\text{-}C_4H_{10},1.0) = -8.066 + 1.100\text{x}10^{-2}T - 4.077\text{x}10^{-6}T^2 - 8.084\text{x}10^{-11}T^3 + 1.880\text{x}10^{-13}T^4$

$\log k_{b+c}(i\text{-}C^4H^{10},10) = -8.470 + 8.036\text{x}10^{-3}T + 4.358\text{x}10^{-8}T^2 - 1.834\text{x}10^{-9}T^3 + 4.299\text{x}10^{-13}T^4$

(W. Tsang, November 1987)

45,5 $i\text{-}C_4H_9 + O \rightarrow i\text{-}C_3H_7 + HCHO$ (a)
$\rightarrow i\text{-}C_3H_7CHO + H$ (b)

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

Comments and Recommendations

There are no data. Our recommendation is based on the work of Hoyermann and Sievert for the branching ratio for n-propyl radical reaction with O atoms. The overall reaction should be close to collisional. This leads to

$k_{a+b} = 1.6x10^{-10}cm^3molecule^{-1}s^{-1}$ and $k_b/k_a = 3$

The uncertainty is a factor of 3. The interesting aspect of the results of Hoyermann and Sievert is the importance of 1,2 hydrogen migration. Ordinarily, one would have expected step a to be the most important channel.

(W. Tsang, June 1987)

References

Hoyermann, K., and Sievert, R., "The Reactions of Alkyl Radicals with Oxygen Atoms: Identification of Primary Products at Low Pressures," Symp. 17, (Combustion Institute, Pittsburgh, PA 1979) 517

45,6 $i\text{-}C_4H_9 + OH \rightarrow C_4H_8 + H_2O$ (a)
$\rightarrow i\text{-}C_4H_9OH$ (b)

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

Comments and Recommendations

There are no data for these reactions. Step (a) is a disproportionation reaction and we recommend a rate constant one-half of that for OH + n-propyl radical,

$k_a = 2x10^{-11}cm^3molecule^{-1}s^{-1}$

We assign a rate constant for the combination process (b) of

$k_b = 4x10^{-11}cm^3molecule^{-1}s^{-1}$

At sufficiently high temperatures, the hot butanol adduct may decompose to form isopropyl and hydroxymethyl radicals. In view of the instability of isobutyl radicals, this is not likely to make any contribution. The uncertainties are factors of 3.

(W. Tsang, June 1987)

45,7 $i\text{-}C_4H_9 + HO_2 \rightarrow i\text{-}C_3H_7 + HCHO + OH$

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

Comments and Recommendations

There are no data. However the mechanism must involve addition followed by decomposition of the adduct. We recommend the rate expression:

$k_{45,7} = 4x10^{-11}cm^3molecule^{-1}s^{-1}$

with an uncertainty of a factor of 2. Note that this is a composite process. Isobutoxy radical is an intermediate and we are assuming rapid decomposition to formaldehyde and isopropyl.

(W. Tsang, July 1987)

45,8 $i\text{-}C_4H_9 + H_2O_2 \rightarrow i\text{-}C_4H_{10} + HO_2$

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, $k/cm^3molecule^{-1}s^{-1}$	Uncertainty factor
$\log K_p = -1.884 + 3140/T + 10180/T^2 - 7.887x10^6/T^3$				
Recommended value			$4.3x10^{-20}T^{2.13}exp(-1456/T)$	3 at 750K, 10 at 300K and 2500K

Comments and Recommendations

There are no data. Our recommendation of

$k_{45,8} = 4.3x10^{-20}T^{2.13}exp(-1456/T)cm^3molecule^{-1}s^{-1}$

is based on the rate constant for the reverse reaction (44,7) and the thermodynamics. The uncertainties are a factor of 3 near 750 K and increase to an order of magnitude at the extremes of 300 and 2500 K.

(W. Tsang, June 1987)

45,10 $i\text{-}C_4H_9 + CH_4 \rightarrow i\text{-}C_4H_{10} + CH_3$

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, $k/cm^3molecule^{-1}s^{-1}$	Uncertainty factor
$\log K_p = -0.581 - 1119/T + 7.973x10^4/T^2 - 1.023x10^7/T^3$				
Recommended value			$3.55x10^{-26}T^{3.72}exp(-4018/T)$	3

Comments and Recommendations

There are no data. The rate expression for the reverse reaction is fairly reliable. In combination with the thermodynamics we recommend the expression

$k_{45,10} = 3.55\times10^{-26}T^{3.72}\exp(-4018/T)\mathrm{cm^3molecule^{-1}s^{-1}}$

with an uncertainty factor of 3. The rate constants for this reaction are very similar to that for ethyl and n-propyl attack on methane.

(W. Tsang, June 1987)

45,11 $i\text{-}C_4H_9 + C_2H_6 \rightarrow i\text{-}C_4H_{10} + C_2H_5$

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, $k/cm^3molecule^{-1}s^{-1}$	Uncertainty factor
$\log K_p = -0.2648 - 96.60/T + 7.467\times10^4/T^2 - 1.243\times10^7/T^3$				
Recommended value			$4.8\times10^{-25}T^{3.7}\exp(-4924/T)$	3

Comments and Recommendations

There are no data. Our recommended expression of

$k_{45,11} = 4.8\times10^{-25}T^{3.7}\exp(-4924/T)\mathrm{cm^3molecule^{-1}s^{-1}}$

is based on the thermodynamics and our rate expression for the reverse reaction (44,17). The rate constants are very close to that for n-propyl attack on ethane. The uncertainty is a factor of 3.

(W. Tsang, June 1987)

45,12 $i\text{-}C_4H_9 + HCHO \rightarrow i\text{-}C_4H_{10} + HCO$

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, $k/cm^3molecule^{-1}s^{-1}$	Uncertainty factor
Recommended value			$5\times10^{-13}\exp(-3270/T)$	3

Comments and Recommendations

There are no data. We recommend the rate expression

$k_{45,12}=5\times10^{-13}\exp(-3270/T)\mathrm{cm^3molecule^{-1}s^{-1}}$

This is based on Metcalfe and Trotman-Dickenson's rate expression of isobutyl radical attack on the aldehydic hydrogen in isovaleraldehyde and is adjusted for the reaction degeneracy and the value for isobutyl radical combination used here. The uncertainty is a factor of 3.

(W. Tsang, June 1987)

References

Metcalfe, E.L., and Trotman-Dickenson, A.F., "The Reactions of Alkyl Radicals. Part VIII. Isobutyl Radicals from the Photolysis of Isovaleraldehyde," J. Chem. Soc., 5072 (1960)

45,15 $i\text{-}C_4H_9 + HCO \rightarrow i\text{-}C_4H_{10} + CO$

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, $k/cm^3molecule^{-1}s^{-1}$	Uncertainty factor
Recommended value			$6x10^{-11}$	1.5

Comments and Recommendations

There are no data. The recent measurements on HCO for a number of simple alkyl radicals (Baggott, et al) leads to our recommendation of

$k = 6x10^{-11}cm^3molecule^{-1}$

which is the measured value for the n-propyl + HCO reaction. The uncertainty is a factor of 1.5. Particularly interesting is the evidence that the combination reaction is less than a factor of 10 of the disproportionation process.

(W. Tsang, June 1987)

References

Baggott, J. E., Frey, H. M., Lightfoot, F. D., and Walsh, R., "Reaction of Formyl Radical with Alkyl Radicals," J. Phys. Chem. 91, 3386 (1987)

45,16 $i\text{-}C_4H_9 + CH_3 \rightarrow i\text{-}C_5H_{12}$ (a)
$\rightarrow i\text{-}C_4H_8 + CH_4$ (b)

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, $k/cm^3molecule^{-1}s^{-1}$	Uncertainty factor
Recommended value			$k_a=3.2x10^{-10}T^{-0.32}$	2
Recommended value			$k_b=1x10^{-11}T^{-0.32}$	2

Comments and Recommendations

There are no data on the rate constants for these reaction. We recommend the following rate expressions

$k_a = 3.2x10^{-10}T^{-0.32}cm^3molecule^{-1}s^{-1}$

$k_b = 1x10^{-11}T^{-0.32}\ cm^3molecule^{-1}s^{-1}$

with an uncertainty of a factor of 2. They are based on our recommendations for the n-propyl + CH_3 reaction, except for a reduction of a factor of 2 for k_b to take into account the reduction in the available number of hydrogen atoms.

(W. Tsang, June 1987)

45,17 $i\text{-}C_4H_9 + C_2H_5 \rightarrow i\text{-}C_4H_8 + C_2H_6$ **(a)**
$\rightarrow i\text{-}C_4H_{10} + C_2H_4$ **(b)**
$\rightarrow i\text{-}C_4H_9\text{-}C_2H_5$ **(c)**

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, k/cm^{3}molecule^{-1}s^{-1}	Uncertainty factor
Gibian, Corley (1973)			$k_a/k_c=0.04$	1.3
review			$k_b/k_c=0.04$	1.3
Recommended value			$k_c=3.4\times10^{-11}$	1.5
Recommended value			$k_a=1.4\times10^{-12}$	2.0
Recommended value			$k_b=1.4\times10^{-12}$	2.0

Comments and Recommendations

There are no measurements on the combination rate constant. From the geometrical mean rule and rate constants for $i\text{-}C_4H_9$ (45,45) and ethyl (17,17) recombination we then derive

$k_c = 3.4\times10^{-11}\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$

with an uncertainty of a factor of 1.5. Combining this with the recommendations of Gibian and Corley on the disproportionation and combination ratio leads to

$k_a = 1.4\times10^{-12}\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$
$k_b = 1.4\times10^{-12}\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$

with an uncertainty of a factor of 2.
(W. Tsang, July 1987)

45,18 $i\text{-}C_4H_9 + C_2H_4 \rightarrow n\text{-}C_3H_7 + i\text{-}C_3H_7$

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, k/cm^{3}molecule^{-1}s^{-1}	Uncertainty factor
Recommended value	>800		$< 5\times10^{-14}\exp(-3072/T)$	3

Comments and Recommendations

There are no data. Our recommendation of

$k_{45,18} = <5\times10^{-14}\exp(-3072/T)\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$

is based on the assumption that addition will be followed by 1-5 hydrogen shift. This will be favored by the six available primmary hydrogens. The new radical can be expected to decompose rapidly. A slower rate constant will be observed if the direct product decomposes at a rate that is much faster than the isomerization process. The rate expression given here is that recommended for the addition of n-propyl radical to ethylene by Kerr and Parsonage. We estimate an uncertainty factor of 3.
(W. Tsang, June 1987)

References

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

45,19 $i\text{-}C_4H_9 + C_2H_3 \rightarrow$ **4-methylpentene-1** (a)
$\rightarrow i\text{-}C_4H_8 + C_2H_4$ (b)
$\rightarrow i\text{-}C_4H_{10} + C_2H_2$ (c)

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, $k/cm^3molecule^{-1}s^{-1}$	Uncertainty factor
Recommended value			k_a=3.4x10^{-11}	2
Recommended value			k_b=1.4x10^{-12}	4
Recommended value			k_c=1.4x10^{-12}	4

Comments and Recommend

There are no data. Our recommendations are based on the isobutyl and ethyl radical reaction. This leads to

k_a = 3.4x$10^{13}$$cm^3molecule^{-1}s^{-1}$
k_b = 1.4x$10^{-12}$$cm^3molecule^{-1}s^{-1}$
k_c = 1.4x$10^{-12}$$cm^3molecule^{-1}s^{-1}$

The uncertainties are factors of 2,4 and 4 respectively. It should be noted that energetically it is possible that the combination product will decompose to allyl and isopropyl and two propylene radicals. Our RRKM calculations show that this does not become significant until temperatures exceed 1300 K. Under these conditions lifetimes of both radicals (45,1) and (19,1) will be so short that combination is not likely to occur.

(W. Tsang, November 1987)

45,20 $i\text{-}C_4H_9 + C_2H_2 \rightarrow C_3H_6 + C_3H_5$

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

Comments and Recommendations

There are no measurements on the rate constants for this reaction. We recommend the rate expression

$$k(i\text{-}C_4H_9 + C_2H_2 \rightarrow C_3H_6 + C_3H_5) = 1.2\text{x}10^{-12}\exp(-4531/T)cm^3molecule^{-1}s^{-1}$$

with an uncertainty of a factor of 3. This is the rate expression for n-propyl reaction with acetylene and is based on a mechanism that involves addition to acetylene followed by rapid 1-5 hydrogen shift and decomposition of the 2-methyl, 4-pentenyl-1 radical under combustion conditions.

(W. Tsang, November 1987)

45,21 $i\text{-}C_4H_9 + C_2H \rightarrow$ 4-methylpentyne-1 (a)

$\rightarrow C_2H_2 + i\text{-}C_4H_8$ (b)

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

Comments and Recommendatios

There are no measurements on the rate constants for these reactions. We estimate that combination k_a will be similar to that for primary radicals or $2x10^{-11}cm^3molecule^{-1}s^{-1}$. For the disproportionation reaction we estimate a rate constant of $1x10^{-11}cm^3molecule^{-1}s^{-1}$. The uncertainties are factors of 2 and 3, respectively. The hot 4-methylpentyne-1 molecules that are formed from combination can decompose under appropriate pressure and temperature conditions. Our RRKM calculations show however that this does not become significant until the temperature is in excess of 1000 K. At these temperatures combination is not likely to be important since the isobutyl radicals will have decomposed.

(W. Tsang, November 1987)

45,22 $i\text{-}C_4H_9 + CH_3CO \rightarrow i\text{-}C_4H_9COCH_3$

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, $k/cm^3molecule^{-1}s^{-1}$	Uncertainty factor
Recommended value			$3.7x10^{-11}$	2

Comments and Recommendations

There are no data. The rate constant for this reaction can be estimated on the basis of the geometric mean rule and our recommended rate constants for the combination of the two radicals, (45,45) and (22,22). This leads to

$k = 3.7x10^{-11}cm^3molecule^{-1}s^{-1}$

The uncertainty is a factor of 2.

(W. Tsang, July 1987)

45,23 $i\text{-}C_4H_9 + CH_3OO \rightarrow i\text{-}C_3H_7 + CH_3O + HCHO$

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

Comments and Recommendations

There are no data. The mechanism most likely involves addition to form the peroxide and under combustion conditions this will be followed by rapid decomposition to form methoxy and the isobutoxy radical. The latter will rapidly decompose to form isopropyl and formaldehyde. We recommend a rate constant for the overall process of $1.6x10^{-11}cm^3molecule^{-1}s^{-1}$ with an uncertainty of a factor of 2.

(W. Tsang, June 1987)

45,24 $i\text{-}C_4H_9 + CH_3O \rightarrow i\text{-}C_4H_{10} + H_2CO$ (a)
$\rightarrow i\text{-}C_4H_9OCH_3$ (b)

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

Comments and Recommendations

There are no data on the rate constants for these processes. We recommend the following rate expressions:

$k_a = 2x10^{-11}cm^3molecule^{-1}s^{-1}$

$k_b = 1x10^{-11}cm^3molecule^{-1}s^{-1}$

This takes into account the propensity of oxygenated radicals to disproportionate and is consistent with our recommendations for n-propyl combination with methoxy. The uncertainty is a factor of 3.

(W. Tsang, July 1987)

45,25 $i\text{-}C_4H_9 + {}^1CH_2 \rightarrow i\text{-}C_3H_7 + C_2H_4$ (a)
$\rightarrow C_2H_5 + C_3H_6$ (b)
$\rightarrow CH_3 + i\text{-}C_4H_8$ (c)

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, $k/cm^3molecule^{-1}s^{-1}$	Uncertainty factor
Recommended value			$k_a=2.4x10^{-11}$	2
Recommended value			$k_b=7.2x10^{-11}$	2
Recommended value			$k_c=1.2x10^{-11}$	2

Comments and Recommendations

There are no data. Singlet methylene is known to insert rapidly into C-H bonds. This will be followed by rapid decomposition of the hot adduct. On the basis of our recommendations for ${}^1CH_2$ reaction with propane (40,25) we recommend:

$k_a = 2.4x10^{-11}cm^3molecule^{-1}s^{-1}$
$k_b = 7.2x10^{-11}cm^3molecule^{-1}s^{-1}$
$k_c = 1.2x10^{-11}cm^3molecule^{-1}s^{-1}$

The uncertainty is a factor of 2.
(W. Tsang, June 1987)

45,26 $i\text{-}C_4H_9 + {}^3CH_2 \rightarrow i\text{-}C_3H_7 + C_2H_4$

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

Comments and Recommendations

There are no data. The main reaction is undoubtedly addition to form a hot isopentyl radical which decomposes rapidly into ethylene and isopropyl radical. The rate constant is

$k = 3x10^{-11}cm^3molecule^{-1}s^{-1}$

The uncertaity is a factor of 2.
(W. Tsang, June 1987)

45,38 $i\text{-}C_4H_9 + CH_3OH \rightarrow i\text{-}C_4H_{10} + CH_2OH$ (a)
$\rightarrow i\text{-}C_4H_{10} + CH_3O$ (b)

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, $k/cm^3molecule^{-1}s^{-1}$	Uncertainty factor
Recommended value			$k_a=5.3x10^{-23}T^{3.17}exp(-4610/T)$	3
Recommended value			$k_b=2.4x10^{-23}T^{3.1}exp(-4510/T)$	3

Comments and Recommendations

There are no data. We suggest the use of the rate expressions which we have recommended for n-propyl attack on methanol, i.e.

$k_a = 5.3\times10^{-23}T^{3.17}\exp(-4610/T)\mathrm{cm}^3\mathrm{molecule}^{-1}\mathrm{s}^{-1}$

$k_b = 2.4\times10^{-23}T^{3.1}\exp(-4500/T)\mathrm{cm}^3\mathrm{molecule}^{-1}\mathrm{s}^{-1}$

The uncertainties are factors of 3.

(W. Tsang, June 1987)

45,39 $i\text{-}C_4H_9 + CH_2OH \rightarrow$ 3-methylbutanol (a)

$\rightarrow i\text{-}C_4H_{10} + CH_2O$ (b)

$\rightarrow i\text{-}C_4H_8 + CH_3OH$ (c)

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, $k/\mathrm{cm}^3\mathrm{molecule}^{-1}\mathrm{s}^{-1}$	Uncertainty factor
Recommended value			$k_a=3.2\times10^{-11}$	2
Recommended value			$k_b=3.2\times10^{-11}$	3
Recommended value			$k_c=0.8\times10^{-12}$	3

Comments and Recommendations

There are no data. We recommend the rate expressions derived from the geometric mean rule and the rate constants for n-propyl (41,41) and hydroxymethyl (39,39) combination. This leads to

$k_a = 3.2\times10^{-11}\mathrm{cm}^3\mathrm{molecule}^{-1}\mathrm{s}^{-1}$

$k_b = 3.2\times10^{-11}\mathrm{cm}^3\mathrm{molecule}^{-1}\mathrm{s}^{-1}$

$k_c = 0.8\times10^{-12}\mathrm{cm}^3\mathrm{molecule}^{-1}\mathrm{s}^{-1}$

where the last rate expression has been lowered by a factor of two from the n-propyl system in order to take into account the reaction degeneracy. The uncertainties are factors of 2, 3 and 3 respectively.

(W. Tsang, November 1987)

45,40 $i\text{-}C_4H_9 + C_3H_8 \rightarrow i\text{-}C_4H_{10} + n\text{-}C_3H_7$ (a)

$\rightarrow i\text{-}C_4H_{10} + i\text{-}C_3H_7$ (b)

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, $k/\mathrm{cm}^3\mathrm{molecule}^{-1}\mathrm{s}^{-1}$	Uncertainty factor
Recommended value			$k_a=1.5\times10^{-24}T^{3.65}\exp(-4600/T)$	3
Recommended value			$k_b=2.5\times10^{-24}T^{3.46}\exp(-3750/T)$	3

Comments and Recommendations

There are no data. We recommend rate expressions similar to that for ethyl attack on propane. This leads to

$k_a = 1.5\times10^{-24}T^{3.65}\exp(-4600/T)\mathrm{cm}^3\mathrm{molecule}^{-1}\mathrm{s}^{-1}$

$k_b = 2.5\times10^{-24}T^{3.46}\exp(-3750/T)\mathrm{cm^3molecule^{-1}s^{-1}}$

The uncertainties are factors of 3.

(W. Tsang, June 1987)

45,41 $i\text{-}C_4H_9 + n\text{-}C_3H_7 \rightarrow n\text{-}C_3H_7 + i\text{-}C_4H_9$ (a)
$\rightarrow C_3H_6 + i\text{-}C_4H_{10}$ (b)
$\rightarrow i\text{-}C_4H_8 + C_3H_8$ (c)

Reference	Conditions Temp./K	[M]/molecule $\mathrm{cm^{-3}}$	Reaction rate constant, $k/\mathrm{cm^3molecule^{-1}s^{-1}}$	Uncertainty factor
Recommended value			$k_a=3.4\times10^{-11}$	1.5
Recommended value			$k_b=2.4\times10^{-12}$	2.0
Recommended value			$k_c=1.2\times10^{-12}$	2.0

Comments and Recommendations

There are no data. From the geometric mean rule we obtain $3.4\times10^{-11}\mathrm{cm^3molecule^{-1}s^{-1}}$ using the combination rates of n-propyl (41,41) and isobutyl (45,45). The disproportionation rate constants are based on the disproportanation to combination ratios of 0.15 for n-propyl and 0.076 for isobutyl. The uncertainties are factors of 1.5, 2.0 and 2.0 respectively.

(W. Tsang, June 1987)

45,42 $i\text{-}C_4H_9 + i\text{-}C_3H_7 \rightarrow (i\text{-}C_4H_9\text{-}i\text{-}C_3H_7$ (a)
$\rightarrow i\text{-}C_4H_8 + i\text{-}C_3H_8$ (b)
$\rightarrow i\text{-}C_4H_{10} + C_3H_6$ (c)

Reference	Conditions Temp./K	[M]/molecule $\mathrm{cm^{-3}}$	Reaction rate constant, $k/\mathrm{cm^3molecule^{-1}s^{-1}}$	Uncertainty factor
Recommended value			$k_a=2.9\times10^{-11}(300/T)^{0.35}$	2
Recommended value			$k_b=0.58\times10^{-11}(300/T)^{0.35}$	2
Recommended value			$k_c=0.32\times10^{-11}(300/T)^{0.35}$	2

Comments and Recommendations

There are no data on the mechanisms and rate constants for these reactions. We recommend the use of our recommendation for n-propyl radical reaction with isopropyl radical (42,41) and correcting for the fewer number of beta hydrogens in the isobutyl radical. This leads to

$k_a=2.9\times10^{-11}(300/T)^{0.35}\mathrm{cm^3molecule^{-1}s^{-1}}$

$k_b/k_a = 0.2$

$k_c/k_a = 0.11$

The uncertainties are factors of 2.

(W. Tsang, November 1987)

45,43 $i\text{-}C_4H_9 + i\text{-}C_4H_{10} \rightarrow i\text{-}C_4H_{10} + t\text{-}C_4H_9$

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, k/cm^{3}molecule^{-1}s^{-1}	Uncertainty factor
Recommended value			$0.9\times10^{-24}T^{3.46}\exp(-3000/T)$	2.5

Comments and Recommendations

There are no measurements on the rate constants for this reaction. We recommend the use of the rate expression for n-propyl attack on the tertiary hydrogen in isobutane (43,41 (a)) or

$k_{45,43} = 0.9\times10^{-24}T^{3.46}\exp(-3000/T)\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$

The estimated uncertainty is a factor 2.5.

(W. Tsang, November 1987)

45,44 $i\text{-}C_4H_9 + t\text{-}C_4H_9 \rightarrow i\text{-}C_4H_9\text{-}t\text{-}C_4H_9$ (a)

$\rightarrow i\text{-}C_4H_{10} + i\text{-}C_4H_8$ (b)

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, k/cm^{3}molecule^{-1}s^{-1}	Uncertainty factor
Recommended value			$k_a=8.3\times10^{-12}(300/T)^{0.75}$	2
Recommended value			$k_b=5.0\times10^{-12}(300/T)^{0.75}$	2

Comments and Recommendations

There have been no measurements on the rate constants for these reactions. Our recommendations are based on the rate expressions for n-propyl radical with t-butyl radical (44,41) and after taking into account the one available hydrogen in isobutyl radical. The rate expressions are

$k_a=8.3\times10^{-12}(300/T)^{0.75}\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$ and $k_b/k_a=0.6$

The uncertainty limits are a factor of 2.

(W. Tsang, November 1987)

45,45 $i\text{-}C_4H_9 + i\text{-}C_4H_9 \rightarrow (i\text{-}C_4H_9)_2$ (a)

$\rightarrow i\text{-}C_4H_8 + i\text{-}C_4H_{10}$ (b)

Reference	Conditions Temp./K	 [M]/molecule cm^{-3}	Reaction rate constant, k/cm^{3}molecule^{-1}s^{-1}	Uncertainty factor
Gibian and Corley (1973) review			$k_b/k_a=0.076$	1.5
Recommended value			$k_a=1.7\times10^{-11}$	1.5
Recommended value			$k_b=1.3\times10^{-12}$	2.0

Comments and Recommendations

There are no data for the combination process. Our recommendation is based on the rate expression for n-propyl recombination (41,41) and the estimated error is a factor of 1.5. The disproportionation rate constant is that derived from Gibian and Corley's work with an uncertainty of a factor of 1.15

(W. Tsang, June 1987)

References

Gibian, M. J., and Corley, R. C., "Organic Radical-Radical Reactions. Disproportionation vs. Combination," Chemical Reviews **73**, 441 (1973).

4. Thermodynamic Data Tables

Thermodynamic properties of isobutane (Species No. 43)

	J mol^{-1} K^{-1}		kJ mol^{-1}	
T/K	C_p	S	Δ_fH	Δ_fG
300	97.28	295.18	−134.68	−20.21
500	149.03	357.52	−148.45	60.21
700	187.65	414.13	−157.36	145.35
900	216.10	464.88	−162.34	232.59
1100	237.69	510.41	−164.35	320.58
1300	254.01	551.53	−164.18	408.73
1500	266.40	588.56	−163.09	498.81

$\log K_p = -23.2928+9213.31/T-360434/T^2+283075/T^3$.

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

Thermodynamic properties of *tert*-butyl radical (Species No. 44)

	J mol^{-1} K^{-1}		kJ mol^{-1}	
T/K	C_p	S	Δ_fH	Δ_fG
300	78.61	320.10	51.88	139.28
500	124.54	370 97	36.49	202.03
700	163.36	419.33	25.66	270.32
900	192.68	464.09	18.87	341.19
1100	214.61	504.99	15.34	413.22
1300	230.99	542.24	13.95	485.65
1500	243.28	576.19	13.82	558.28

$\log K_p = -19.4278 + 415.205/T - 728375/T^2 + 5.1014\times10^7/T^3$.

Frequencies (degeneracy) 2931(6), 2825(3), 1455(6), 1370(3), 1279(1),1252(2), 1189(2), 1126(1), 992(2), 733(1), 541(2), 200(1); 3 free rotor with $I = 4.7 \times 10^{-40}$ gm cm^2 and symmetry 3. Moment of Inertia, 2.246×10^{-114} gm cm^2, symmetry 3; ground state degeneracy 2.

J. H. Purnell and C. P. Quinn, J. Chem. Soc., 4049, (1964); W. Tsang, J. Amer. Chem. Soc. **107**, 2782 (1985).

Thermodynamic properties of isobutyl radical (Species No. 45)

	J mol^{-1} K^{-1}		kJ mol^{-1}	
T/K	C_p	S	Δ_fH	Δ_fG
300	96.19	320.87	69.45	156.65
500	142.05	380.58	57.61	218.27
700	176.10	434.72	49.87	284.26
900	201.63	481.87	44.79	351.96
1100	221.08	524.17	42.83	419.73
1300	235.52	562.20	42.45	488.44
1500	246.40	596.60	43.44	557.59

$\log K_p = -18.1538 - 1643.12/T - 363581.7/T^2 + 10717452/T^3$.

Frequencies (degeneracy); 3020(2), 2950(6), 2820(1), 1460(5), 1377(2), 1355(2), 1200(1), 1172(1), 1098(1), 965(2), 921(2), 799(1), 550(1), 437(1), 371(2); 1 free rotors, $I=3.5 \times 10^{-40}$ gm cm^2 with symmetry 2. 2 hindered rotors. $I=4.9 \times 10^{-40}$ gm cm^2 with symmetry number 3 and barrier to internal rotation, 15 kJ; Moment of Inertia, 1.92×10^{-114} gm cm^2, symmetry 1; ground state degeneracy; 2.

J. Pacansky, D. W. Brown and J. S. Chang, J. Chem. Phys. **85**, 2562 (1981).
W. Tsang, J. Amer. Chem. Soc. **107**, 2872 (1985).

5. Transport Properties

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

Substance	d 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	3.626	481.8
Propane	5.118	237.1
n-Propyl	5.118	237.1
iso-Propyl	5.118	237.1
Isobutane	5.278	330.1
t-Butyl	5.278	330.1
iso-Butyl	5.278	330.1

Values for stable species are from R. C. Reid, J. M. Prausnitz, and B. E. Poling, "The Properties of Gases and Liquids" (3rd. ed.) McGraw-Hill Book Company, New York, (1987).

Values for the radicals are assummed to be same as that for the molecules from which they are derived