

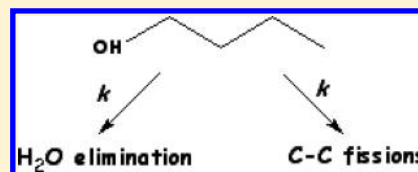
Shock Tube Study on the Thermal Decomposition of *n*-Butanol

Claudette M. Rosado-Reyes* and Wing Tsang

National Institute of Standards and Technology, Gaithersburg, Maryland 20899, United States

Supporting Information

ABSTRACT: Dilute concentrations of normal-butanol has been decomposed in single pulse shock tube studies in the presence of large quantities of a chemical inhibitor that suppresses contributions from chain decomposition. Reaction temperatures and pressures are in the range of [1126–1231] K and [1.3–6.5] bar. Ethylene and 1-butene are the only products. The mechanism of the initial decomposition steps involves direct elimination of water and C–C bond cleavage. The fundamental high pressure unimolecular decomposition rate expressions are $k(\text{C}_4\text{H}_9\text{OH} \rightarrow \text{CH}_3 + \text{CH}_2\text{CH}_2\text{CH}_2\text{OH}) = 10^{16.4 \pm 0.4} \exp(42410 \pm 800 [\text{K}]/T) \text{ s}^{-1}$; $k(\text{C}_4\text{H}_9\text{OH} \rightarrow \text{CH}_3\text{CH}_2 + \text{CH}_2\text{CH}_2\text{OH}) = 10^{16.4 \pm 0.4} \exp(-41150 \pm 800 [\text{K}]/T) \text{ s}^{-1}$; $k(\text{C}_4\text{H}_9\text{OH} \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2 + \text{CH}_2\text{OH}) = 10^{16.4 \pm 0.4} \exp(-41150 \pm 800 [\text{K}]/T) \text{ s}^{-1}$; and $k(\text{C}_4\text{H}_9\text{OH} \rightarrow \text{CH}_3\text{CH}_2\text{CH}=\text{CH}_2 + \text{H}_2\text{O}) = 10^{14.0 \pm 0.4} \exp(-35089 \pm 800 [\text{K}]/T) \text{ s}^{-1}$, where the rate expressions for C–C bond cleavage are based on assumptions regarding the relative rates of the three processes derived from earlier studies on the effect of an OH group on rate expressions. All reactions are in the high pressure limit and suggest that the step size down in the presence of argon is at least 1300 cm^{-1} . These rate expressions are consistent with the following H–C bond dissociation energies: $\text{BDE}(\text{H}-\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}) = 417.2 \pm 7 \text{ kJ/mol}$, $\text{BDE}(\text{H}-\text{CH}_2\text{CH}_2\text{OH}) = 419.2 \pm 7 \text{ kJ/mol}$, and $\text{BDE}(\text{H}-\text{CH}_2\text{OH}) = 401.7 \pm 9 \text{ kJ/mol}$, with an estimated uncertainty of 6 kJ/mol. The kinetics and thermodynamic results are compared with estimates used in the building of combustion kinetics databases.



1. INTRODUCTION

Interest in biofuels has led to the consideration of alcohols such as *n*-butanol as a fuel. Biofuels are oxygenated compounds rather than hydrocarbons as in conventional fossil fuels and represent a renewable energy source. *n*-Butanol is more attractive over ethanol as a replacement for gasoline because of its higher energy density closer to gasoline is less volatile and corrosive, and more hydrophobic. Acetone–butanol–ethanol (ABE) process¹ has been the most widely used method to produce butanol via the bacterial fermentation of starch by using the micro-organism *Clostridium acetobutylicum*. However, the isolation of alcohol from the ABE blend is difficult and requires distillation, resulting in low alcohol yields and production. The development of more economically viable strategies that enable the production of biofuels has led to the design of novel metabolic engineering approaches that utilize glucose as renewable carbon source to produce higher alcohols (C₄–C₅).²

Interest in butanol as a biofuel has inspired considerable new work on its combustion properties such as flame speeds or ignition delays. We term these global properties because the measurements represent the combination of all the thermodynamic and kinetic properties that lead to a particular result. Complete combustion kinetic mechanisms have been postulated in order to fit the observations. Although there are results from ab initio calculations and estimates on the basis of rate rules,³ there are no experimental studies (to our knowledge) on the rate constants and expressions for the fundamental chemical kinetics. The present work is aimed to support the combustion models and, more importantly, furnish information that tests the reliability of ab initio calculations at various levels

of theory as well as estimates based on rate rules. The elimination of water from *n*-butanol is a particularly interesting case. It is a complex process involving the simultaneous breaking and forming of a number of chemical bonds. Since it involves the formation of stable compounds, it is straightforward to study this type of reaction in single pulse shock tube experiments.

The emphasis on fundamental processes is due to the fact that there is no possible scenario for using a particular biofuel by itself. Instead, it will always be used in mixtures with other hydrocarbon fuel molecules. The study of fundamental chemical processes of individual fuel molecules is imperative to eventually understand the behavior of fuel mixtures. The only transferable data in such contexts are those of a fundamental nature. Such data are the basis for establishing rate rules that permit the extrapolation and interpolation of combustion properties to a wider variety of real fuel systems. Since it is not possible to measure every possible rate constant, properly calibrated theoretical calculations will ultimately be the basis of the rate rules used in compiling combustion kinetic databases.

This work presents the first time a larger primary alcohol is being studied in the laboratory under the high temperature conditions characteristic of combustion, where branching ratio for dehydration versus bond cleavage is unambiguously determined from direct product detection and analysis. Most of the high temperature fundamental experimental data dealing

Received: May 25, 2012

Revised: August 29, 2012

Published: August 30, 2012

Table 1. Rate Expressions for the Decomposition of Various Alcohols^a

	k (s ⁻¹)	reference
Water Elimination		
<i>tert</i> -butanol → <i>i</i> -butene + H ₂ O	$3.98 \times 10^{14} \exp(-33288/T)$	Lewis et al. (1974) ⁵
2,3-dimethylbutanol-2 → 2,3-dimethylbutene-1 + H ₂ O	$10^{14.17} \exp(-32300/T)$	Tsang (1976) ⁴
2,3-dimethylbutanol-2 → 2,3-dimethylbutene-2 + H ₂ O	$10^{13.66} \exp(-32700/T)$	Tsang (1976) ⁴
3,3-dimethylbutanol-2 → 2,3-dimethylbutene-1 + H ₂ O	$10^{14.0} \exp(-34200/T)$	Tsang (1976) ⁴
<i>n</i> -butanol → 1-butene + H ₂ O	$9.9 \times 10^{13} \exp(-35089/T)$	this work
	$1.0 \times 10^{14} \exp(-34038/T)$	Grana et al. (2010) ¹⁵
	$2.0 \times 10^{14} \exp(-36254/T)$	Moss et al. (2008) ¹⁷
C–C Fissions		
<i>n</i> -butanol → CH ₃ + CH ₂ CH ₂ CH ₂ OH	$2.5 \times 10^{16} \exp(-42410/T)$	this work
	$2.0 \times 10^{16} \exp(-43303/T)$	Grana et al. (2010) ¹⁵
	$5.82 \times 10^{15} \exp(-42734/T)$	Moss et al. (2008) ¹⁷
	$7.1 \times 10^{16} \exp(-43414/T)$	Dagaut et al. (2008) ¹⁶
<i>n</i> -butanol → C ₂ H ₃ + CH ₂ CH ₂ OH	$2.5 \times 10^{16} \exp(-41150/T)$	this work
	$2.0 \times 10^{16} \exp(-42800/T)$	Grana et al. (2010) ¹⁵
	$2.23 \times 10^{15} \exp(-41672/T)$	Moss et al. (2008) ¹⁷
	$5.0 \times 10^{16} \exp(-43188/T)$	Dagaut et al. (2008) ¹⁶
<i>n</i> -butanol → <i>n</i> C ₃ H ₇ + CH ₂ OH	$2.5 \times 10^{16} \exp(-41150/T)$	this work
	$2.0 \times 10^{16} \exp(-42800/T)$	Grana et al. (2010) ¹⁵
	$1.47 \times 10^{15} \exp(-41757/T)$	Moss et al. (2008) ¹⁷
	$2.4 \times 10^{16} \exp(-43188/T)$	Dagaut et al. (2008) ¹⁶

^aUnits: E_a/R (K); E_a (cal/mol).

with primary alcohols relate to methanol and ethanol. We have previously reported on the decomposition of a number of substituted highly branched secondary alcohols,⁴ 2,3-dimethylbutanol-2 and 3,3-dimethylbutanol-2. There have also been reports on the decomposition of *tert*-butanol.⁵ All of the results are summarized in Table 1. In comparison to a pure hydrocarbon, possible channels for alcohol decomposition are (1) direct water elimination, introducing an olefin into the system and (2) carbon–carbon bond fission. Depending on the magnitude of the rate constants, they define the reaction pathway of subsequent reaction processes. This should help establish the general trends for water elimination from alcohols. It would be of great interest to know how this work compares to a halide system that might be thought of as analogous and if the same rules apply to alcohols. Four center molecular elimination processes are well-known processes for hydrogen halide elimination from alkyl halides.⁶ The rate constants and parameters are highly dependent on methyl substitution, suggestive of a strongly ionic transition state.

The other possible processes for decomposition are carbon–carbon bond cleavages. Note that the binding energy of the carbon–OH bond is at least 42 kJ/mol higher than that of the C–C bond. If the A-factors are similar, this is equivalent to rate constants that are 2 orders of magnitude slower than the corresponding C–C bond cleavage. The rate constants that have been determined from the earlier work on the highly branched alcohols⁴ indicate that the addition of OH has an effect on the rate constant for C–C bond breaking similar to CH₃ substitution. This observation will be necessary in the subsequent product analysis.

The present work is an extension of the earlier studies on the decomposition of hydrocarbon fuels. We have previously carried out similar experiments with alkanes and alkyl radicals. These have given definitive results on the cracking of these molecules and fragments. The special features of these studies consist on the use of a single pulse shock tube, the presence of the target molecule in trace concentrations, and the use of a

chemical scavenger in large excess to inhibit radical induced decompositions. These features also permit the use of an internal standard to determine reaction temperature. Since the reaction mechanism is unambiguously set by the use of the inhibitor, the determination of the reaction temperature by internal standard makes it possible to obtain unimolecular rate constants and through its molecular properties for the breakdown of hydrocarbons and their fragments. This work on the decomposition of *n*-butanol involves a considerably smaller molecule and raises the possibility that energy transfer effects, or not enough collisions to achieve a Boltzmann distribution, may perturb the experimentally measured rate expressions and thus lead to rate expressions that may be smaller than the high pressure values. We have noted that, for the smallest fuels studied, neopentane⁷ and 2,3-dimethylbutane,⁸ as examples, the rate parameters are all slightly smaller than expected.

This work will demonstrate that the shock tube technique is ideal for studying the thermal stability behavior of the individual compounds in real fuel mixtures. Real fuels are the fuels used in combustion devices and are complex mixtures of hydrocarbons. The present methodology, where all stable products are detected, allows the determination of reaction mechanisms for larger size organic molecules because they leave stable fragments that can only be attributed to unimolecular decompositions. Thus, for example, there are contributions from roaming radicals⁹ leading to alternative channels and the unimolecular formation of saturated organic compounds as opposed to unimolecular formation of radicals.

2. EXPERIMENTAL METHODS

Experiments were carried out in a heated single pulse shock tube. Details and procedures can be found in earlier publications.^{7,8,10,11} The reader is referred to these papers for a thorough discussion of the procedures used and the unique capabilities regarding the accurate determination of rate constants for unimolecular processes that are obtained. For

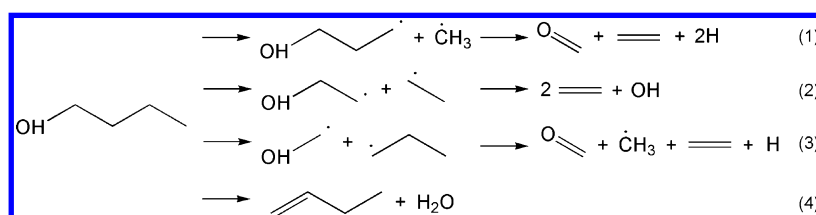


Figure 1. Reaction mechanism for *n*-butanol thermal decomposition.

product analysis from *n*-butanol decomposition, simultaneous gas chromatography coupled with flame ionization and mass spectral detection and analysis are performed after the separation of the postshock mixture components. Flame ionization detection (FID) peak areas are converted into molar quantities using molar responses determined from standard samples. Adequate FID signal response was obtained for the purpose of the analysis. The accuracy of the concentrations of products determined is of the order of 5%. The concentration of reactants and extent of reaction were set to achieve this limit.

The samples used in the present studies involve 500 $\mu\text{L/L}$ (0.05%) of *n*-butanol and 10000 $\mu\text{L/L}$ (1%) of 1,3,5-trimethylbenzene. The latter is used as chemical inhibitor. The following are the considerations that justify the claim that, with these concentration ratios, practically all chain processes are eliminated. 1,3,5-Trimethylbenzene has nine abstractable hydrogens and a stable benzylic type radical is formed when subjected to radical attack. Because of the weak benzylic C–H bond, this benzylic radical cannot abstract hydrogens from *n*-butanol in the time scale of these experiments. Instead, its primary removal channel is through combination with the radicals in the system, primarily methyl and benzylic radicals. The more reactive radicals such as H and OH are removed by abstraction of the benzylic hydrogen. Reactions were carried out with initial pressures of 0.1 and 0.4 bar. This is equivalent to a final pressure in the reflected shock of 1.5 to 6.5 bar, calculated from the after-shock (reaction) temperature and mixture composition via the ideal shock equations.¹² The temperature was determined on the basis of the internal standard method. The standard reaction consists on the reverse Diels–Alder decomposition of 4-methylcyclohexene (4MCH). The rate expression is¹³

$$k(4\text{-methylcyclohexene} \\ \rightarrow \text{propene} + 1, 3\text{-butadiene}) \\ = 10^{15.26} \exp(-66800[\text{cal/mol}]/RT) \text{ s}^{-1}$$

This rate expression has been used in all comparative rate single pulse shock tube experiments. Because of the exponential dependence of the rate constant on temperature, this is an extremely precise method for determining the reaction temperature. Scatter of results is drastically reduced. This reaction involves the direct formation of stable products. Hence, there are no radical induced products, and very accurate rate expression is readily determined. Detailed uncertainty analysis can be found in standard reviews.¹⁰ The use of the same internal standard makes it possible to derive correlations that can lead to predictions. From the disappearance of 4MCH, one can derive a reaction temperature from the following relationships:

$$k(\text{experimental}, \text{s}^{-1}) = \tau^{-1} \ln([4\text{MCH}]_0/[4\text{MCH}]\tau)$$

$$T(\text{experimental}, \text{K}) = (E_a/R)/(\ln A - \ln k),$$

$$\text{where } \tau = 0.0005 \text{ s}$$

n-Butanol was obtained from Sigma-Aldrich and used without further purification. Gas chromatographic analysis did not reveal the presence of any impurities.

The use of the internal standard removes all the inherent uncertainties in the physical properties in these shock tube experiments as determined from the conservation equations. The major uncertainty is the reaction temperature. The relatively high concentration of larger polyatomic compounds will introduce large uncertainties in any calculated reaction temperature. The introduction of the internal standard removes this uncertainty since both the internal standard and target molecule experience the same temperature, heating time, and reaction pressures. The most striking contrast in comparison to determination of the reaction temperature by solving the conservation equations is the reduction in scatter. With the high concentrations of polyatomic molecules, the deviation in temperature will vary depending on the extent of reaction. There is also cancellation of errors in the residence time. Generally speaking, it will be difficult to obtain quantitative results under the conditions of these experiments without an internal standard.

3. RESULTS

The only detectable products from the decomposition of *n*-butanol are ethylene and 1-butene. These studies are carried out from low to higher conversions. Under the former conditions, mass balance considerations are not meaningful. The reaction mechanism by which these products are formed is shown in Figure 1. Methyl radicals and hydrogen atoms are scavenged by 1,3,5-trimethylbenzene or by recombination reactions. Our mechanism should yield a considerable amount of formaldehyde formed as a result of CH_2OH radical decomposition. Formaldehyde is insensitive to FID detection. Attempts at detection using the mass spectrometric signal were unsuccessful except as the highest conversions, due to the decreased sensitivity. The four-centered water elimination (Reaction 4 in Figure 1) is the only source of 1-butene in our experiments. Figure 2 contains a plot of the ethylene/1-butene ratio as a function of temperature. It can be seen that this ratio increases with temperature and hence is consistent with the ethylene channel having stronger temperature dependence than that for 1-butene formation.

n-Butanol decomposition also takes place via three different C–C bond fission pathways. All three C–C bond cleavage channels lead to the production of ethylene. Thus, it is not possible to distinguish between the three channels without ancillary information. The ancillary information that we use in the data analysis is that the rate constants for reactions 2 and 3 are similar to each other. This is based on the earlier observation, on the decomposition of branched alcohols⁴ that

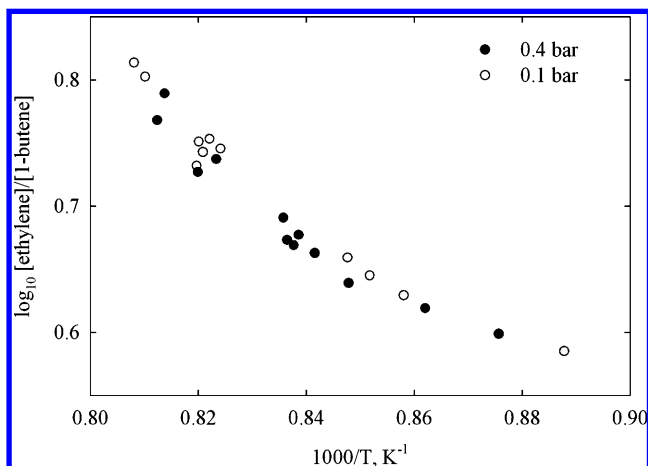


Figure 2. Branching ratio of C–C bond fission versus water elimination from the experimental yields of ethylene and 1-butene.

the interchange of OH and CH₃ groups has a similar effect on the rate constants. Similarly,¹⁰ substitution in the beta position has no effect on the rate constant for the C–C bond being broken. On the basis of the relative concentrations measured earlier.^{4,10} We estimate that these assumptions have an uncertainty of a factor of 1.2. Reaction 1 has a smaller rate constant since it involves the ejection of a methyl group, and its rate constant will be smaller than that of reaction 2 and 3 by the factor of $\exp(-2500[\text{cal/mol}]/RT)$, based on earlier work on hydrocarbons.¹⁰ This is directly related to experimental observations from comparative rate single pulse shock tube work. It contrasts with literature estimates of relative rates based on independent measurements. These estimates are difficult to compare accurately as a result of mechanistic artifacts and even small uncertainties in the reaction temperatures.

Reaction 2 produces two ethylene molecules, and reaction 3 produces only one ethylene molecule. The following deduced stoichiometry permits the apportioning of the total experimental ethylene yield by the factors of $\exp(-2500[\text{cal/mol}]/RT)$, 2, and 1, for reactions 1, 2, and 3, respectively. On this basis, we obtain the Arrhenius plots as given in Figures 3–5. The rate constants are determined on the basis of the standard relationship¹⁰ for a multichannel process. Thus, for a

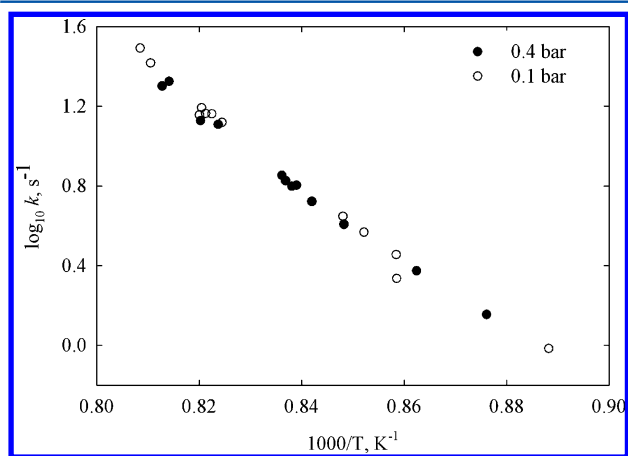


Figure 3. Arrhenius plot for the formation of ethylene via C₁–C₂ bond scission, ejecting a methyl group upon cleavage, during *n*-butanol thermal decomposition; reaction 1.

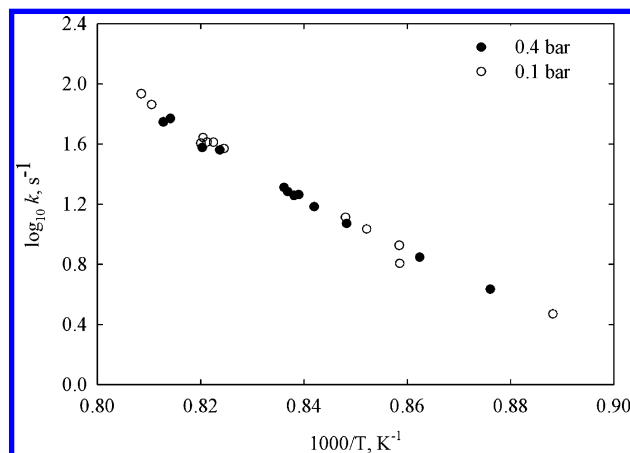


Figure 4. Arrhenius plot for the formation of ethylene via C₂–C₃ and C₃–C₄ bond scissions during *n*-butanol thermal decomposition; reactions 2 and 3.

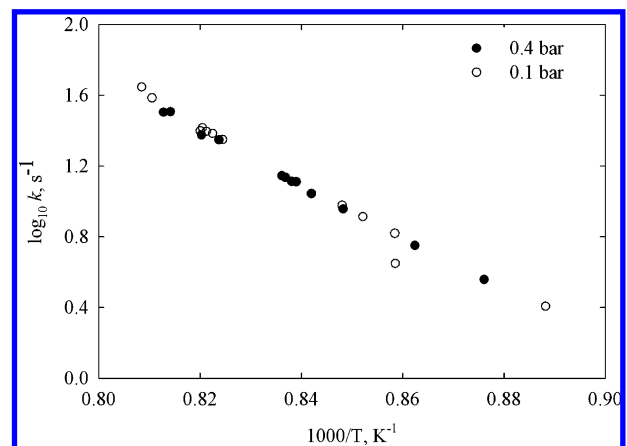


Figure 5. Arrhenius plot for the formation of 1-butene via 1,2-water elimination during *n*-butanol thermal decomposition; reaction 4.

multichannel decomposition of the type studied here, the rate constant for each individual channel can be written in terms of the total rate constant

$$k_{\text{total}} = -1/\tau \ln[1 - (\sum \text{product}_i/\text{reactant}_0)]$$

where the total rate constant k_{total} is the sum of all the individual rate constants, and τ is the residence of 500 μs . The individual rate constant (k_i) can then be expressed as

$$k_i = k_{\text{total}} \times (\text{product}_i/\sum \text{product}_i)$$

where the subscript i refers to the various channels that are part of the products assigned to the ethylene yield that is experimentally detected, normalized over the initial *n*-butanol concentration. The maximum conversion of *n*-butanol that we obtained during the experiments was 13%. Note that, in order to unambiguously establish the mechanism, reactions were carried out to much higher conversion. The 13% refers to the data used in the analysis. The Arrhenius rate expressions for all processes are as follow:

$$k_1 = 10^{16.4 \pm 0.4} \exp(-42410 \pm 800[\text{K}]/T) \text{ s}^{-1}$$

$$k_2 = 10^{16.4 \pm 0.4} \exp(-41150 \pm 800[\text{K}]/T) \text{ s}^{-1}$$

$$k_3 = 10^{16.4 \pm 0.4} \exp(-41150 \pm 800[\text{K}]/T) \text{ s}^{-1}$$

$$k_4 = 10^{14.0 \pm 0.4} \exp(-35089 \pm 800[\text{K}]/T) \text{ s}^{-1}$$

The uncertainties given here include, to a large extent, the possible errors from the slope measurements. They are somewhat larger because these results are dependent on the method for partitioning the ethylene yields among the three channels as described above. For the present purposes, changing the mechanism will lead to one rate constant being larger and the other smaller. Since the total ethylene yield is fixed, the maximum change on the partitioned ethylene rate expressions is a factor of 2 if all the ethylene should come from a single channel, which is an unlikely possibility.

A significant consequence of the present observations is the failure to observe any pressure dependence over the pressure range studied. Note that, with the internal standard method, very small pressure dependence should be detectable. We estimate in the most conservative fashion that differences in rate constants in two comparative rate experiments with the same internal standard of the order of 5–10% should be readily detectable.

4. DISCUSSION

The rate expressions for bond cleavage can be readily converted to bond energies and, through it, the enthalpies of the oxygenated radicals that are formed. Thus, for reactions 2 and 3, we find

$$\begin{aligned} \Delta H_2 &= \Delta H_3 \\ &= \Delta E + RT \\ &= E_a [\text{J/mol}] + (8.314[\text{J}/(\text{K}\cdot\text{mol})] \times 1100[\text{K}]) \end{aligned}$$

Assuming that the reverse process has no activation energy, we find the heat of formation of the hydroxymethyl, 2-hydroxyethyl radical, and 3-hydroxypropyl radicals at 300 K to be -17.9 , -33.5 , and -58.6 kJ/mol, with the appropriate heat capacity correction. This is based on the well established heat of formation of ethyl and propyl radical to be 118 and 98.7 kJ/mol. The bond dissociation energies at 300 K are then $\text{BDE}(\text{H}-\text{CH}_2\text{OH}) = 401.7 \pm 9$ kJ/mol, $\text{BDE}(\text{H}-\text{CH}_2\text{CH}_2\text{OH}) = 419.2 \pm 7$ kJ/mol, and $\text{BDE}(\text{H}-\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}) = 417.2 \pm 7$ kJ/mol. The former is in excellent agreement with the experiment and review of Johnson and Hudgens.¹⁴ $\text{BDE}(\text{H}-\text{CH}_2\text{OH})$ and $\text{BDE}(\text{H}-\text{CH}_2\text{CH}_2\text{OH})$ are very close to the H–R bond energy where R is ethyl or propyl. The thermochemistry is therefore close to the estimated uncertainties derived from this type of kinetic measurements or on the order of 6 kJ/mol, from the numbers derived in this study. The somewhat larger uncertainty estimates given here takes into account the assumptions on the branching ratios for ethylene mentioned earlier. This may be in the same range as the best ab initio calculations for small species such as hydroxymethyl. It is interesting that the effect of OH for CH_3 substitution is much larger for the breaking of C–H bonds in comparison to C–C bonds. The present results indicates that the empirical rate rules used in deriving these results have considerable validity and therefore are extensible to related molecules.

Figure 6 contains a very interesting comparison in the rate constants for water elimination from a number of alcohols,^{4,5,15} including elimination from primary, secondary, and tertiary alcohols. We have neglected all data about ethanol because the

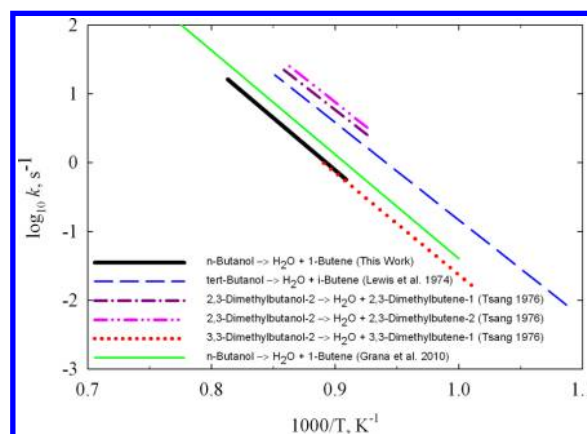


Figure 6. Arrhenius plot for the reaction of alcohol \rightarrow H_2O + olefin (per H atom β to OH).

data is ambiguous due to the formation of ethylene from both water elimination and chain processes. A considerable variation in the estimated rate constants for the elimination of water is observed. The most interesting consequence of this work is the lack of sensitivity of water elimination to methyl substitution, specially observed between the cases of *n*-butanol (this work) and 3,3-dimethylbutanol-2.⁴ In the case of HX elimination from the alkyl halide, methyl substitution leads to drastic increases in rate constants under temperatures slightly lower than those used here.⁶ Indeed, the results parallel to some degree the situation in solution and hence the conclusion that the transition state is likely to be semi-ionic in character. It would be extremely interesting to examine theoretically the transition state for water elimination and compare it with the situation for the alkyl halides. The estimate by Grana et al.¹⁵ is in close agreement with our direct measurement. However, their justification for their selection in terms of analogies with the alkyl halides is not valid. The determination of an energy barrier for water elimination of 67.26 kcal/mol by Moc et al.³ via ab initio calculations [CCSD(T)/cc-pVTZ//MP2/6-311G-(d,p)] is also in good agreement with our experimental determination of 69.5 kcal/mol.

Comparison of estimated rate constants for *n*-butanol decomposition via C–C fission can be found in Figure 7. There are considerable variations in the estimated rate constants in the modeling studies^{15–17} versus those determined in this work. Unfortunately, the methodology of how such estimates are made is often unclear. The heats of formation appear to be within the error bars of the present experiments. There appears to be some uncertainty in the high pressure rate expressions. It may well be that these uncertainties do not affect various combustion properties. Nevertheless, they send a cautionary note on the use of ab initio or other methods in estimating rate constants for combustion related reactions.

We do suspect that a factor of 3 to 10 is a reasonable assignment of uncertainties to such estimates. A particularly accurate measurement is our ethylene to 1-butene ratio. This may be of importance in certain applications since it involves the formation of radicals and an olefin. The latter through the formation of a resonance stabilized radical can serve as an important chain terminator. This is directly seen in Figures 6 and 7 where the differences in rate constants between molecular elimination and bond breaking are displayed. Note that the estimates of Grana et al.¹⁵ would make the water elimination process much more important than our directly

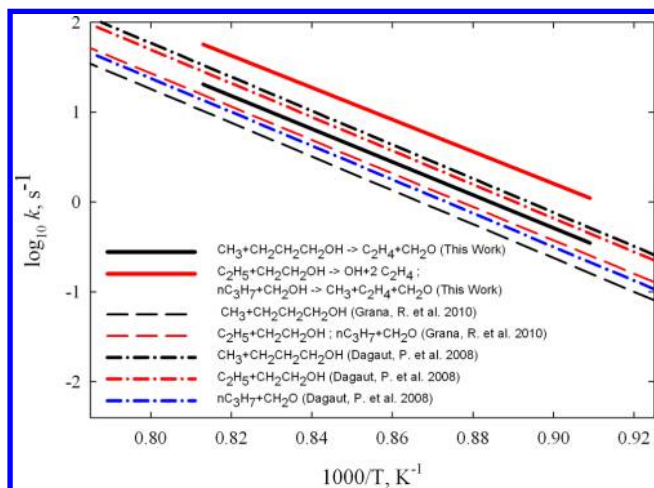


Figure 7. Rate constants for *n*-butanol decomposition pertaining unimolecular initiation reactions; comparison of this work with modeling studies.

measured number. Here again, the effect on global properties is uncertain. We are planning to carry out a detailed uncertainty analysis for this system.

In an earlier section, we have mentioned the absence of pressure effect in *n*-butanol decomposition. Except for CF_3Br (where a pressure effect was observed), this is the smallest molecule that has been studied in our single pulse shock tube. We have accordingly carried out RRKM calculations in order to establish the consequences with respect to the magnitude of the energy transfer parameter consonant with this observation. Our procedure is guided by the experimental finding that the measured rate constants have no or minimal measured pressure dependence. Thus, transition states are defined to match experimental observations. That is what the rate parameters exactly reproduced. Note that possible curvature in the Arrhenius plots is only a property of the high-pressure rate constant. RRKM calculations will reveal the possible pressure dependence. Results on the high-pressure rate constants can be found in Figure 8 and on the fall-off behavior of the unimolecular channels in Figure 9. It appears that a minimum step size down of $\Delta E = 1300 \text{ cm}^{-1}$ or larger is required to fit the experimental observations of no or minimal observed pressure dependence. This step size is a factor of 2 larger than

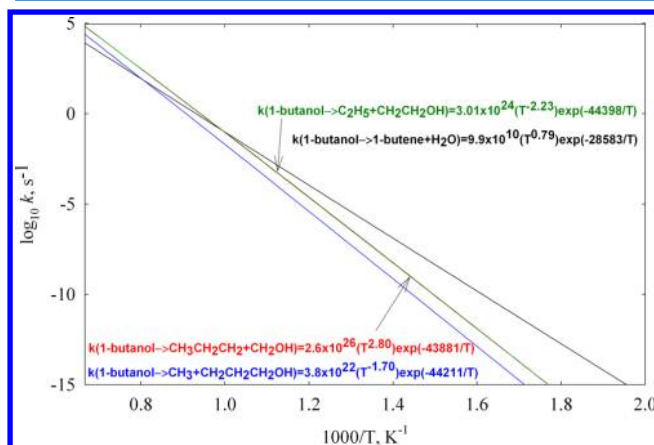


Figure 8. High-pressure rate constants for *n*-butanol decomposition derived from RRKM calculations.

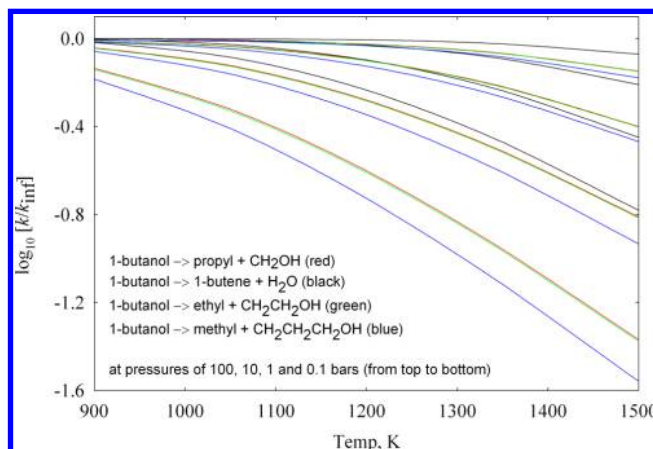


Figure 9. Fall-off behavior of unimolecular processes during *n*-butanol thermal decomposition.

for comparable hydrocarbon systems. It may well be that the presence of the OH group has a major effect on the propensity for energy transfer.

5. CONCLUSIONS

We have experimentally determined the rate expressions for all the channels contributing to *n*-butanol decomposition, under conditions where only unimolecular decomposition can occur. The rate expressions for the multichannel decomposition processes have been found to be

$$k(\text{C}_4\text{H}_9\text{OH} \rightarrow \text{CH}_3 + \text{CH}_2\text{CH}_2\text{CH}_2\text{OH}) = 10^{16.4 \pm 0.4} \exp(-42410 \pm 800[\text{K}]/T) \text{ s}^{-1}$$

$$k(\text{C}_4\text{H}_9\text{OH} \rightarrow \text{CH}_3\text{CH}_2 + \text{CH}_2\text{CH}_2\text{OH}) = 10^{16.4 \pm 0.4} \exp(-41150 \pm 800[\text{K}]/T) \text{ s}^{-1}$$

$$k(\text{C}_4\text{H}_9\text{OH} \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2 + \text{CH}_2\text{OH}) = 10^{16.4 \pm 0.4} \exp(-41150 \pm 800[\text{K}]/T) \text{ s}^{-1}$$

$$k(\text{C}_4\text{H}_9\text{OH} \rightarrow \text{CH}_3\text{CH}_2\text{CH}=\text{CH}_2 + \text{H}_2\text{O}) = 10^{14.0 \pm 0.4} \exp(-35089 \pm 800[\text{K}]/T) \text{ s}^{-1}$$

Comparison with analogous systems is provided. Under our experimental conditions of [1126–1231] K and [1.5–6.5] bar, no pressure dependence was observed. This was verified by RRKM calculations, if standard assumptions on the step size down parameter are used. The present results provide a basis for the prediction of the rate constant of some of the initial steps in the decomposition on *n*-butanol. It would be extremely interesting to determine their effects on the global properties (that are a conglomerate of many rate constants) that are usually determined in combustion experiments. As mentioned earlier, this is particularly important for the chemical behavior of real fuel mixtures where only correct rate constant values can lead to the proper mixing rules.

■ ASSOCIATED CONTENT

Supporting Information

Examples of gas chromatograms of postshock mixtures and tabulated raw measured data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

AUTHOR INFORMATION

Notes

The authors declare no competing financial interest. Certain commercial materials and equipment are identified in this article to specify adequately the experimental procedure. In no case does such identification imply recommendation of endorsement by the National Institute of Standards and Technology nor does it imply that the material or equipment is necessarily the best available for the purpose.

REFERENCES

- (1) Lee, S. Y.; Park, J. H.; Jang, S. H.; Nielsen, L. K.; Kim, J.; Jung, K. *S. Biotechnol. Bioeng.* **2008**, *101*, 209–228.
- (2) Atsumi, S.; Hanai, T.; Liao, J. C. *Nature* **2008**, *451*, 86–90.
- (3) Moc, J.; Simmie, J. M.; Curran, H. J. *J. Mol. Struct.* **2009**, *928*, 149–157.
- (4) Tsang, W. *Int. J. Chem. Kinet.* **1976**, *8*, 173–192.
- (5) Lewis, D.; Keil, M.; Sarr, M. *J. Am. Chem. Soc.* **1974**, *96*, 4398–4404.
- (6) Maccoll, A.; Thomas, P. J. *Nature* **1955**, *176*, 392–393.
- (7) Tsang, W. *J. Chem. Phys.* **1966**, *44*, 4283–4295.
- (8) Tsang, W. *J. Chem. Phys.* **1965**, *43*, 352–359.
- (9) Harding, L. B.; Klippenstein, S. J. *J. Phys. Chem. Lett.* **2010**, *1*, 3016–3020.
- (10) Tsang, W.; Lifshitz, A. *Annu. Rev. Phys. Chem.* **1990**, *41*, 559–599.
- (11) Tsang, W. *J. Chem. Phys.* **1964**, *41*, 2487–2494.
- (12) Gaydon, A. G.; Hurler, I. R. *The Shock Tube in High-Temperature Chemical Physics*; Reinhold Publishing: New York, 1963.
- (13) Tsang, W. *J. Chem. Phys.* **1965**, *43*, 1805–1809.
- (14) Johnson, R. D., III; Hudgens, J. W. *J. Phys. Chem.* **1996**, *100*, 19874–19890.
- (15) Grana, R.; Frassoldati, A.; Faravelli, T.; Niemann, U.; Ranzi, E.; Seiser, R.; Cattolica, R.; Seshadri, K. *Combust. Flame* **2010**, *157*, 2137–2154.
- (16) Dagaut, P.; Togbé, C. *Fuel* **2008**, *87*, 3313–3321.
- (17) Moss, J. T.; Berkowitz, A. M.; Oehlschlaeger, M. A.; Biet, J.; Warth, V.; Glaude, P. A.; Battin-Leclerc, F. *J. Phys. Chem. A* **2008**, *122*, 10843–10855.