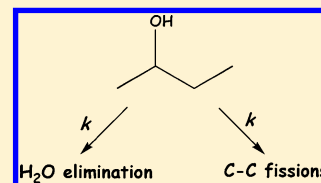


Shock Tube Studies on the Decomposition of 2-Butanol

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ABSTRACT: The thermal decomposition of 2-butanol have been studied at temperatures of 1045–1221 K and pressures of 1.5–6 bar using the single pulse shock tube technique. Dilute concentrations of 2-butanol have been decomposed in the presence of large quantities of a radical inhibitor. The mechanism for decomposition involves direct elimination of water producing *cis*- and *trans*-2-butene, and 1-butene, and C–C bond fission producing ethylene. Acetaldehyde, propionaldehyde, and propene were also observed in much smaller yields from C–C bond fission. The respective unimolecular rate expressions are as follows: $k(\text{C}_3\text{H}_6(\text{OH})\text{CH}_3 \rightarrow \text{cis-CH}_3\text{CH}=\text{CHCH}_3 + \text{H}_2\text{O}) = 10(13.1 \pm 0.3) \exp(-33414 \pm 755 \text{ K}/T) \text{ s}^{-1}$; $k(\text{C}_3\text{H}_6(\text{OH})\text{CH}_3 \rightarrow \text{trans-CH}_3\text{CH}=\text{CHCH}_3 + \text{H}_2\text{O}) = 10(13.5 \pm 0.3) \exp(-33820 \pm 755 \text{ K}/T) \text{ s}^{-1}$; $k(\text{C}_3\text{H}_6(\text{OH})\text{CH}_3 \rightarrow \text{CH}_3\text{CH}_2\text{CH}=\text{CH}_2 + \text{H}_2\text{O}) = 10(13.6 \pm 0.3) \exp(-33002 \pm 755 \text{ K}/T) \text{ s}^{-1}$; $k(\text{C}_3\text{H}_6(\text{OH})\text{CH}_3 \rightarrow \text{C}_2\text{H}_5\cdot + \cdot\text{CH}(\text{OH})\text{CH}_3) = 10(15.9 \pm 0.3) \exp(-39252 \pm 755 \text{ K}/T) \text{ s}^{-1}$. These rate expressions are compared with analogous reactions for primary and tertiary butanols. They form a basis for the prediction of those for related systems. Comparison with estimated values used in the simulation of butanol combustion is indicative of the uncertainties in the rate constants that are used in such models. The activation energy of 326 kJ/mol leads to a bond dissociation energy of the $\text{CH}(\text{OH})\text{CH}_3$ radical ($\text{H}-\text{CH}(\text{OH})\text{CH}_3$) of 400 kJ/mol, in excellent agreement with earlier calculated results from theory and disagreement with the experimental results from iodination studies in the expected range.



INTRODUCTION

There have been many recent studies on the use of butanols as fuels in combustion processes.^{1–6} Many of these studies have attempted to simulate the behavior of such systems using fundamental single step chemical reactions. This paper is concerned with the initial unimolecular decomposition of 2-butanol. It is an extension of our earlier work on *n*-butanol.⁷ Our interest is in the rate expressions of the breakdown processes when 2-butanol is subject to high temperature combustion environments.

This work is designed to help provide fundamental or transferable information on the chemical kinetics of biofuels combustion. This will bring such databases to the same level as those for the petroleum based fuels that are widely used in computer simulations. The emphasis on fundamental information arises from the practical need of ultimately dealing with fuel mixtures. Fundamental information represents data that lead directly to mixing rules that cannot be determined on any other basis. Any possible use of biofuels will be in combination with petroleum based substances. The greatest difference in the fundamental reaction processes between any two fuels is the initial radical formation and destruction processes. Once the primary radicals are formed upon initial thermal decomposition, their subsequent reactions become increasingly similar as combustion progresses, ultimately leading to the production of carbon dioxide, water or soot.

The determination of the rate expressions for the chemical processes involved in fuel breakdown during combustion has increasingly dependence on the use of ab initio calculations for estimations. The uncertainties in these estimations are somewhat unclear. This is especially the case as the fuel molecules become larger. An added complication is the many different theory approaches utilized in making such estimates.

Thus unambiguous experimental results are important not only for the purposes of simulations but also as a basis for calibrating theoretical calculations.

For the present study we use a well established methodology that has been previously employed to study the fundamental kinetics of the decomposition of many intermediate size organic fuels⁸ and more recently the fuel radicals that are the first products⁹ from fuel decomposition. These results provide the basic information from which the rate expressions of such processes for all petroleum based compounds can be estimated. These numbers are generally accepted and used in the most recent combustion kinetics databases such as JetSurf.¹⁰ The present work concentrates on the effect of introducing an OH group into the basic hydrocarbon framework.

The experiments were carried out in a heated single pulse shock tube. The key features of these experiments are the dilute concentrations of the test mixture, of the order of 500 $\mu\text{L}/\text{L}$, and the presence of large excesses of a chemical inhibitor, 1% 1,3,5-trimethylbenzene. The chemical inhibitor captures all the reactive radicals that are formed. Thus only the unimolecular reaction contributes to the product yields. The isolation of the unimolecular reaction from all other processes means that it is possible to simultaneously study other unimolecular reactions whose rate expression for decomposition are well established in the same system. Thus for the extent of decomposition an average temperature of the system can be determined using an internal standard approach makes certain that the nonidealities in the shock tube study are experienced by both target molecules. Therefore, results from the shock tube study are

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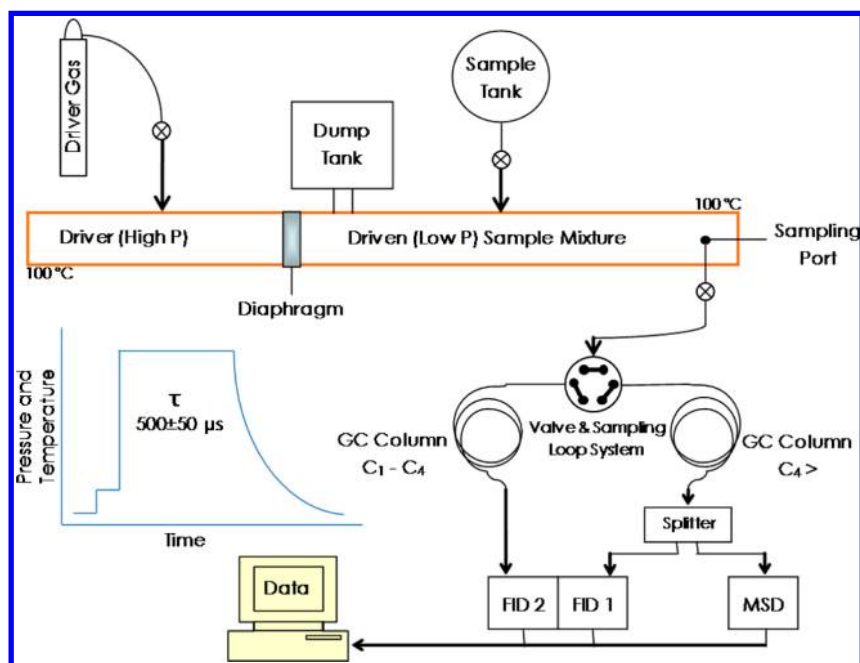


Figure 1. Schematic illustration of the shock tube apparatus and components.

traceable and transferable and provide the basic information necessary for developing the relationships between the behaviors of all fuels that have been studied.

We have previously studied the decomposition of *n*-butanol.⁷ Ethylene and 1-butene are the main detectable products. The rate expressions for all the possible decomposition pathways are

$$k(\text{C}_4\text{H}_9\text{OH} \rightarrow \text{CH}_3 + \text{CH}_2\text{CH}_2\text{CH}_2\text{OH}) \\ = 2.5 \times 10^{16} \exp(-42410 \text{ K}/T) \text{ s}^{-1}$$

$$k(\text{C}_4\text{H}_9\text{OH} \rightarrow \text{CH}_3\text{CH}_2 + \text{CH}_2\text{CH}_2\text{OH}) \\ = 2.5 \times 10^{16} \exp(-41150 \text{ K}/T) \text{ s}^{-1}$$

$$k(\text{C}_4\text{H}_9\text{OH} \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2 + \text{CH}_2\text{OH}) \\ = 2.5 \times 10^{16} \exp(-41150 \text{ K}/T) \text{ s}^{-1}$$

$$k(\text{C}_4\text{H}_9\text{OH} \rightarrow \text{CH}_3\text{CH}_2\text{CH}=\text{CH}_2 + \text{H}_2\text{O}) \\ = 1.0 \times 10^{14} \exp(-35089 \text{ K}/T) \text{ s}^{-1}$$

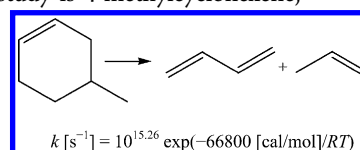
Of particular interest is the rate expression for the direct elimination of water. This reaction must involve a four-center transition state. The rate expression for direct water elimination from 1-butanol is in disagreement with results derived from ab initio calculations¹¹ and on a per H-atom basis is surprisingly close to that for *tert*-butanol.¹ This is contrary to what one would expect on the basis of other four-center elimination processes involving alkyl halides where elimination of HCl is drastically affected by alkyl substitution.¹² The concerted water elimination process involving the simultaneous breaking and formation of number of bonds would seem to provide a crucial test of the accuracy of appropriate ab initio calculations of transition state properties. The bond breaking reactions involve assumptions regarding the distribution of ethylene from the three possible channels and are based on the effect of OH substitution from the decomposition of more highly branched

butanols. These assumptions will be confirmed with the product distribution obtained from 2-butanol pyrolysis.

EXPERIMENTAL METHODS¹³

The thermal decomposition of 2-butanol has been induced in a heated single pulse shock tube. A schematic of the instrument can be found in Figure 1. A brief description of the shock tube scheme is provided. The shock tube consists of two sections, a 171 cm driven section and 125 cm driver section, built from 3.2 cm² i.d. aluminum tubing, separated by a cellophane diaphragm. Upon the rupture of the diaphragm, a shock wave is created, which subjects the test gas to adiabatic compression and heating during two temperature steps, first by the incident wave and second by the reflected wave from the end wall. The shock-heated gas remains at temperature for about $500 \pm 50 \mu\text{s}$ prior to rapid quenching by the dump tank. Immediately after, an undiluted gas sample is extracted into two valves and sampling loops, where it is compressed to typically 1 bar, and the injected into two individual GC columns for simultaneous separation of the mixture components and analysis. Lighter gases (C_1 – C_4) are more efficiently separated in a Restek 30 m \times 0.53 mm i.d. Rt-Alumina capillary column, coupled with a back-flushable precolumn to trap heavy species and prevent contamination. Heavier gas components are well separated in a J&W Scientific 30 m \times 0.53 mm i.d. DB-1 fused silica column. Simultaneous flame ionization and mass spectral detection and analysis are performed after the separation of the mixture components. FID peaks areas are converted into molar quantities using molar responses determined from standard samples.

Experimental studies were carried out with a mixture concentration of 500 $\mu\text{L}/\text{L}$ 2-butanol in 1.0% 1,3,5-trimethylbenzene. The internal temperature standard used in the present study is 4-methylcyclohexene,¹⁴



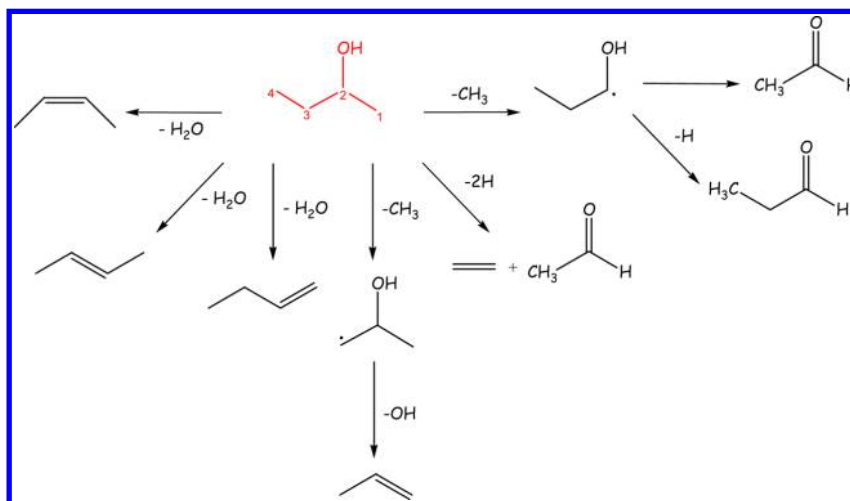


Figure 2. Proposed reaction mechanism for the thermal decomposition of 2-butanol.

From this rate expression one obtains the following reaction temperature as function of the product yield,

$$T_{\text{exp}} [\text{K}] = (E_a/R)/(\ln A - \ln k_{\text{exp}})$$

where the experimental rate for the internal standard decomposition is defined as

$$k_{\text{exp}} [\text{s}^{-1}] = \tau^{-1} \ln([std]_0/[std]_t)$$

and τ is the residence time of about 500 μs . Note that the internal standard reaction is purely molecular in nature. Thus radicals cannot be released into the system. The concentration of standard used in these studies was 200 $\mu\text{L/L}$.

The thermal decomposition of 2-butanol was examined in the absence and presence of the temperature standard. This permits an estimate to be made of the concentration of propene formed from 2-butanol decomposition because propene is also formed from the decomposition of the temperature standard. Because an equal amount of 1,4-butadiene and propene was found from the decomposition of the standard we found that a small amount of propene was indeed formed from the decomposition of the 2-butanol. The aftershock temperature was then determined from the formation of 1,3-butadiene and confirmed by the disappearance of 4-methylcyclohexene.

Shock pressures are calculated from the experimental temperature and mixture composition via ideal shock equations. Chemicals were purchased from Sigma-Aldrich Chemicals. Gas chromatography did not uncover any impurities and the samples were therefore used without purification.

Aftershock experimental conditions of 1045–1221 K in temperature and 1.5–6 bar in pressures were achieved.

RESULTS

The major stable products detected from 2-butanol decomposition are ethylene, *trans*-2-butene, *cis*-2-butene, 1-butene, propene, and acetaldehyde. There is evidence that propionaldehyde is also present. Ethylene and propene along with the aldehydes are the expected products following the initial cleavage of the C–C bonds. The butenes can only arise from 1,2-elimination of water from the 2-butanol. Note that with the OH in the secondary position, 1-butene can only be formed from the abstraction of a primary H-atom whereas the 2-butenes are formed from secondary hydrogen. The relative yields and rate expressions should therefore lead to interesting

information regarding the nature of the transition state for this type of elimination process. Also found were methane and ethane, from methyl and H radical recombination and methyl self-reaction, respectively. H and CH_3 fragments are scavenged by the excess of 1,3,5-trimethylbenzene. A detailed breakdown of the decomposition of 2-butanol, including water elimination and C–C bond breaking channels, is given in Figure 2. The processes that are considered for analysis are those that lead to the formation of the butenes, ethylene, and propene.

Excellent GC separation was obtained between *cis*-2-butene, *trans*-2-butene, and 1-butene in both GC columns, making them unique markers for concerted 1,2-elimination of water. They provide a basis for comparison with the earlier work on 1-butanol and branched butanols. The overall process is a typical multichannel unimolecular decomposition reaction. Rate parameters were derived easily because the formation of all the hydrocarbon products were clearly monitored by the GC. The following rate expressions were derived for 1045–1221 K and 1.5–6 bar, where the degree of conversion of the temperature standard was up to 61%, and that for the 2-butanol was 30%. This leads to the following rate expressions,

$$\begin{aligned} k(\text{C}_3\text{H}_6(\text{OH})\text{CH}_3 \rightarrow \textit{cis}\text{-CH}_3\text{CH}=\text{CHCH}_3 + \text{H}_2\text{O}) \\ = 1.41 \times 10^{13} \exp(-33414 \text{ K}/T) \text{ s}^{-1} \end{aligned}$$

$$\begin{aligned} k(\text{C}_3\text{H}_6(\text{OH})\text{CH}_3 \rightarrow \textit{trans}\text{-CH}_3\text{CH}=\text{CHCH}_3 + \text{H}_2\text{O}) \\ = 2.90 \times 10^{13} \exp(-33820 \text{ K}/T) \text{ s}^{-1} \end{aligned}$$

$$\begin{aligned} k(\text{C}_3\text{H}_6(\text{OH})\text{CH}_3 \rightarrow \text{CH}_3\text{CH}_2\text{CH}=\text{CH}_2 + \text{H}_2\text{O}) \\ = 3.57 \times 10^{13} \exp(-33002 \text{ K}/T) \text{ s}^{-1} \end{aligned}$$

$$\begin{aligned} k(\text{C}_3\text{H}_6(\text{OH})\text{CH}_3 \rightarrow \text{C}_2\text{H}_5\cdot + \cdot\text{CH}(\text{OH})\text{CH}_3) \\ = 7.40 \times 10^{15} \exp(-39252 \text{ K}/T) \text{ s}^{-1} \end{aligned}$$

The respective Arrhenius plots, for the water elimination channels and $\text{C}_2\text{--C}_3$ during 2-butanol decomposition are shown in Figures 3 and 4.

The kinetic information for the $\text{C}_2\text{--C}_3$ bond scission reaction of 2-butanol is based on the yield of ethylene. Note that ethylene is the only compound that can be formed from this process. Therefore, there can be little ambiguity regarding the derived rate expression. This is unlike the situation for 1-

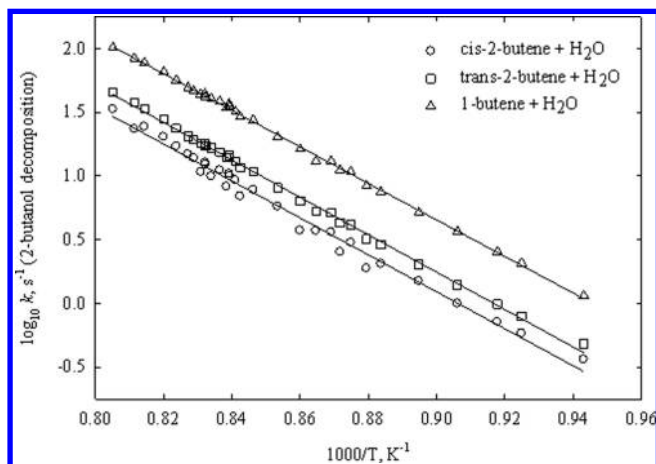


Figure 3. Arrhenius plots for the decomposition of 2-butanol into the different water elimination channels.

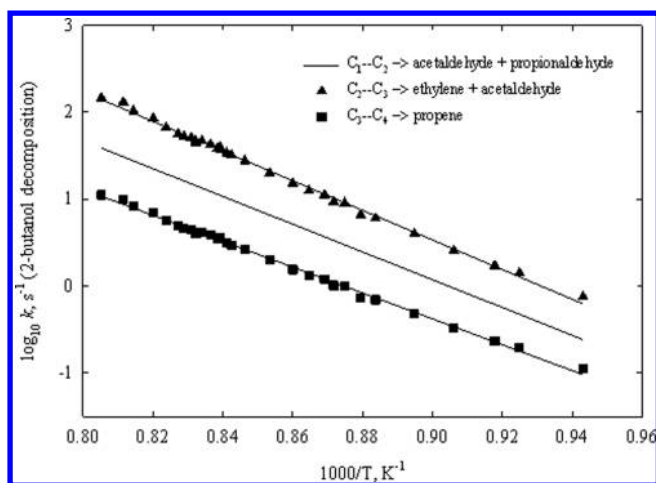


Figure 4. Arrhenius plots for the decomposition of 2-butanol via C–C bond fission.

butanol where ethylene can be derived from all the C–C bond cleavage reactions.

It is assumed that the ethyl radical is quantitatively converted to ethylene and the hydroxyl ethyl radical is not transformed to ethylene. These are very valid assumptions. The lifetime of ethyl radicals under the present conditions is less than a few microseconds. We assume that 1,2 isomerization of the hydroxyl ethyl radical is much slower than H-atom ejection. Note that H-atom ejection will in all cases lead to the formation of acetaldehyde.

Our analysis of acetaldehyde was not satisfactory. To establish the relative sensitivity of acetaldehyde to ethylene, experiments were carried out on the thermal decomposition of ethyl vinyl ether, which is known to decompose via a retroene reaction to form equal amounts of ethylene and acetylene. From these experiments we observed lesser amounts of acetaldehyde than expected and the amount of acetaldehyde seems to decrease with the total yields of ether decomposing. We plan to return to this issue in the subsequent reports. Note that the absence of pressure dependence in the rate constants in all the experiments with 2-butanol mean that all the rate expressions directly determined are true unimolecular rate expressions.

We have attempted to relate propene yields as a consequence of propene formation from C₃–C₄ bond cleavage. As we can be seen from Figure 2, this can be only formed upon methyl ejection followed by the very fast unimolecular decomposition of the 2-hydroxypropyl radical through the β bond cleavage of the C–OH bond. This is thermodynamically favored over the breaking of the C–CH₃ bond. A key problem in the interpretation of the results is the small yields of propene or roughly one tenth of the ethylene formed. The relationship between ethylene and propene yields can be found in Figure 5. Following the procedure outlined above we obtain the following rate expression,

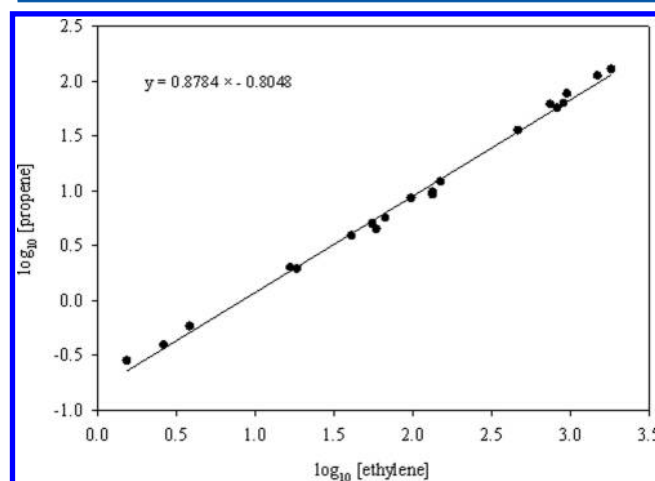
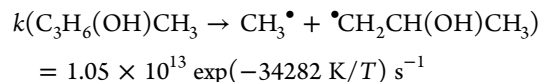


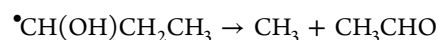
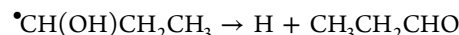
Figure 5. Molar yields of ethylene plotted against those of propene, in the absence of temperature standard.

The A-factor and activation energy are far smaller than what would be expected for the CH₃–C bond dissociation energy. One suspects that there may be other sources of propene from impurity in the system. A plot of the rate constant can be found in Figure 4 and shows the relative unimportance of the C₁–C₂ reaction in comparison to the C₂–C₃ channel. At the present time, propene is not considered in the product analysis, along with ethylene, 1-butene, and 2-butene.

A final process involves the cleavage of the C₁–C₂ bond. The process is



Our analytical procedure does not permit us to assess the yields arising from methyl radicals. The 1-hydroxypropyl radical can decompose via the following processes,



As noted above, we have been able to detect small amount of propionaldehyde. Acetaldehyde was also formed in larger amounts from C₂–C₃ bond cleavage. Thus there is not sufficient data to give a quantitative measure of the contribution from this channel. From earlier correlations it is clear that this will be substantially smaller than that from the main bond breaking channel. We have accordingly chosen to ignore

contributions from this channel in the quantitative analysis of the data. This is justified by the low extent ($\sim 30\%$) of 2-butanol decomposition in the studies.

DISCUSSION

All our numerical results on the reported rate expressions are based on the hydrocarbons experimentally detected: 1-butene, *trans*-2-butene, *cis*-2-butene, and ethylene. These products will also be basis for the estimated rate expressions that will be presented in the following discussion.

The results on the propene yields have rate expressions that are incompatible with bond breaking, with the actual rate constants about an order of magnitude smaller than the C_2-C_3 process. If we assume as noted earlier that this is brought about by small contributions from additional sources forming propene, we find that with a standard A -factor of 10^{16} s^{-1} then at an average temperature of 1160 K this will be equivalent to a rate expression of $10^{16} \exp(-42\,000 \text{ K}/T) \text{ s}^{-1}$. This is very close to the rate expression for losing a methyl group from *n*-butanol.

The present results demonstrate that the thermal decomposition of 2-butanol takes place mainly via the concerted 1,2-elimination of water to produce *trans*-2-butene, *cis*-2-butene, and 1-butene, and via C_2-C_3 bond fission to produce ethylene and acetaldehyde. Rate expressions for these four channels have been derived from the experimental yields of ethylene and the three different butenes. Figure 6 shows the temperature

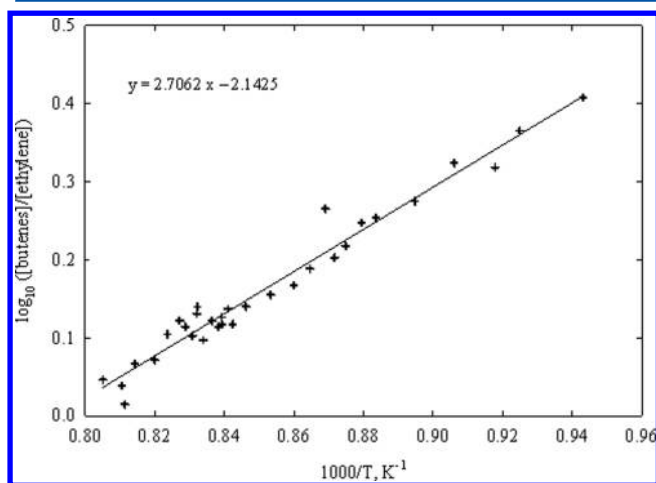


Figure 6. Temperature dependence on the branching ratio of water elimination versus C–C fission.

dependency on the branching ratio of water elimination versus C–C bond fission, $\log_{10} [\sum(\textit{trans}-2-butene, *cis*-2-butene, 1-butene)/ethylene] vs $1/T$. The formation of ethylene via C_2-C_3 fission approaches that of the elimination processes only at the highest temperatures. At the lowest temperature the water elimination reaction accounts for approximately 70% of 2-butanol decomposition.$

For water elimination data, Figure 3 show preferences of 1-butene > *trans*-2-butene > *cis*-2-butene. The yields are only slightly in favor of the 1-butene in comparison to the sum of the two 2-butenes. This is proportional to the number of available hydrogens. The temperatures are very close to those where *cis*–*trans* isomerization of the 2-butenes is occurring. So it is unclear whether this ratio (*cis* to *trans*) is a direct reflection of the nature of the transition states.

Probably the most important consequence of the present work is the possibility of making comparison with the wide number of estimates that now exist in the literature, compiled in Table 1. The results are given in Figure 7 for the elimination of water from 2-butanol to form 1-butene and 2-butene, respectively. They give very good estimates of the range of validity of estimates when compared with the direct measurements. They serve as very important basis for making uncertainty estimates of combustion processes insofar as they are related to input parameters that are not directly determined. Figure 7 represents an attempt at correlating all the shock tube results in terms of the influence of the elimination of primary and secondary OH groups. For completeness we have also included the data on the elimination of tertiary OH group. The important general conclusion is that the position of the OH group has much less influence on elimination of water than for that for the elimination of the I, Br and Cl groups. It suggests that the transition state will have much less ionic character than for the halides.

Figure 8 contains comparison of all the data bearing on the breaking of the C_2-C_3 bond in 2-butanol. The general spread of the results from the estimates mirrors results for the elimination process in terms of excellent agreement in one particular case compared to deviations of an order of magnitude.

It is interesting to compare the rate constants for C_2-C_3 bond cleavage in 1-butanol and 2-butanol. The results can be seen in Figure 9. It can be seen that the addition of the OH group adjacent to the bond being broken leads to larger rate constants. This is in accord with our earlier results in more highly branched alcohols. The ratio of the two rate constants is

$$k(n\text{-butanol})/k(2\text{-butanol}) = 2.2 \times \exp(-1803 \text{ K}/T)$$

This is equivalent to a factor of 40–50% smaller for the 1-butanol. This is very close to the situation for the more highly substituted alcohols studies many years ago. This demonstrates directly the advantage of the comparative rate experiments because direct comparisons can be made.

The present results can be used as a direct measure of the C_2-C_3 bond energy. Assuming that the reverse process has no activation energy and proceeding in the usual manner one begins with,

$$\begin{aligned} \Delta H_{2-3} &= \Delta E_{2-3} + RT \\ &= \text{activation energy [J/mol]} \\ &\quad + (8.314 \text{ J/(K}\cdot\text{mol)}) \times 1160 \text{ [K]} \\ &= 326.3 + 9.6 \\ &= 335.9 \text{ kJ/mol} \end{aligned}$$

With a heat of formation of ethyl radical as 118 kJ/mol (300 K) and 99.5 kJ/mol (1160 K), we find that the heat of formation of the 1-hydroxyethyl radical at 1160 K to be -71.8 kJ/mol . This leads to a value of -52.5 kJ/mol at 300 K. The bond dissociation energy at 300 K is then $\text{BDE}(\text{H}-\text{CHOHCH}_3) = 400 \text{ kJ/mol}$. The only experimental values that we are aware of are those of Alfassi and Golden.¹⁵ They yielded values of -64.4 kJ/mol . This is in accord with past comparisons with other systems that lead to the conclusion that the technique employed by Alfassi and Golden leads to BDE that are 10–20 kJ/mol lower than the actual values. Additional comparisons can be made with the theoretical results of Curtiss

Table 1. Rate Expressions for Various Butanols^a

	k, s^{-1}	ref
Water Elimination		
<i>tert</i> -butanol \rightarrow isobutene + H ₂ O	$3.98 \times 10^{14} \exp(-33288/T)$	Lewis et al. (1974) ¹
2,3-dimethylbutanol-2 \rightarrow 2,3-dimethylbutene-1 + H ₂ O	$10^{14.17} \exp(-32300/T)$	Tsang (1976) ²
2,3-dimethylbutanol-2 \rightarrow 2,3-dimethylbutene-2 + H ₂ O	$10^{13.66} \exp(-32700/T)$	Tsang (1976)
3,3-dimethylbutanol-2 \rightarrow 2,3-dimethylbutene-1 + H ₂ O	$10^{14.0} \exp(-34200/T)$	Tsang (1976)
<i>n</i> -butanol \rightarrow 1-butene + H ₂ O	$1.0 \times 10^{14} \exp(-35089/T)$	Rosado-Reyes and Tsang ⁷
	$1.0 \times 10^{14} \exp(-34038/T)$	Grana et al. (2010) ⁵
	$2.0 \times 10^{14} \exp(-36254/T)$	Moss et al. (2008) ³
2-butanol \rightarrow <i>cis</i> -2-butene + H ₂ O	$1.41 \times 10^{13} \exp(-33414/T)$	this work
2-butanol \rightarrow <i>trans</i> -2-butene + H ₂ O	$2.90 \times 10^{13} \exp(-33820/T)$	this work
\rightarrow <i>cis</i> -2-butene + H ₂ O	$1.78 \times 10^{14} \exp(-35141/T)$	El-Nahas et al. (2011) ⁶
\rightarrow <i>trans</i> -2-butene + H ₂ O	$1.03 \times 10^{14} \exp(-34768/T)$	El-Nahas et al. (2011)
2-butanol \rightarrow (<i>cis</i> + <i>trans</i>)-2-butene + H ₂ O	$1.0 \times 10^{14} \exp(-33283/T)$	Grana et al. (2010)
	$2.0 \times 10^{14} \exp(-33736/T)$	Moss et al. (2008)
2-butanol \rightarrow 1-butene + H ₂ O	$3.57 \times 10^{13} \exp(-33002/T)$	this work
	$1.5 \times 10^{14} \exp(-33787/T)$	Grana et al. (2010)
	$1.5 \times 10^{15} \exp(-33233/T)$	Moss et al. (2008)
	$9.80 \times 10^{13} \exp(-34084/T)$	El-Nahas et al. (2011)
C–C Fissions		
<i>n</i> -butanol \rightarrow CH ₃ + CH ₂ CH ₂ CH ₂ OH \rightarrow HC(O)H + C ₂ H ₄ + H ₂	$2.5 \times 10^{16} \exp(-42410/T)$	Rosado-Reyes and Tsang ⁷
<i>n</i> -butanol \rightarrow CH ₃ + CH ₂ CH ₂ CH ₂ OH	$2.0 \times 10^{16} \exp(-43303/T)$	Grana et al. (2010)
	$5.82 \times 10^{15} \exp(-42734/T)$	Moss et al. (2008)
	$7.1 \times 10^{16} \exp(-43414/T)$	Dagaut et al. (2008) ⁴
<i>n</i> -butanol \rightarrow C ₂ H ₅ + CH ₂ CH ₂ OH \rightarrow 2C ₂ H ₄ +OH	$2.5 \times 10^{16} \exp(-41150/T)$	Rosado-Reyes and Tsang ⁷
<i>n</i> -butanol \rightarrow C ₂ H ₅ + CH ₂ CH ₂ OH	$2.0 \times 10^{16} \exp(-42800/T)$	Grana et al. (2010)
	$2.23 \times 10^{15} \exp(-41672/T)$	Moss et al. (2008)
	$5.0 \times 10^{16} \exp(-43188/T)$	Dagaut et al. (2008)
<i>n</i> -butanol \rightarrow <i>n</i> -C ₃ H ₇ + CH ₂ OH \rightarrow HC(O)H + C ₂ H ₄ + CH ₃ + H	$2.5 \times 10^{16} \exp(-41150/T)$	Rosado-Reyes and Tsang ⁷
<i>n</i> -butanol \rightarrow <i>n</i> -C ₃ H ₇ + CH ₂ OH	$2.0 \times 10^{16} \exp(-42800/T)$	Grana et al. (2010)
	$1.47 \times 10^{15} \exp(-41757/T)$	Moss et al. (2008)
	$2.4 \times 10^{16} \exp(-43188/T)$	Dagaut et al. (2008)
2-butanol \rightarrow CH ₃ + CH ₃ CH ₂ CH(OH) \rightarrow CH ₃ CH ₂ C(O)H + CH ₃ C(O)H	$2.79 \times 10^{14} \exp(-36767/T)$	this work
2-butanol \rightarrow CH ₃ + CH ₃ CH ₂ CH(OH)	$2.0 \times 10^{16} \exp(-43807/T)$	Grana et al. (2010)
	$1.58 \times 10^{15} \exp(-40166/T)$	Moss et al. (2008)
	$4.36 \times 10^{18} \exp(-43560/T)$	El-Nahas et al. (2011)
2-butanol \rightarrow C ₂ H ₅ +CH ₃ CH(OH) \rightarrow C ₂ H ₄ + CH ₃ C(O)H	$7.40 \times 10^{15} \exp(-39252/T)$	this work
2-butanol \rightarrow C ₂ H ₅ +CH ₃ CH(OH)	$2.0 \times 10^{16} \exp(-43555/T)$	Grana et al. (2010)
	$6.06 \times 10^{14} \exp(-41375/T)$	Moss et al. (2008)
	$2.06 \times 10^{19} \exp(-42422/T)$	El-Nahas et al. (2011)
2-butanol \rightarrow CH ₃ + CH ₂ CH(OH)CH ₃ \rightarrow OH + CH ₃ CH=CH ₂	$1.05 \times 10^{13} \exp(-34282/T)$	this work
	$2.0 \times 10^{16} \exp(-43807/T)$	Grana et al. (2010)
	$1.83 \times 10^{15} \exp(-42986/T)$	Moss et al. (2008)
	$8.21 \times 10^{18} \exp(-36767/T)$	El-Nahas et al. (2011)

^aUnits: E_a/R [K].

et al.¹⁶ The present results are in excellent agreement. However, for all this type of shock tube results, it is estimated that the absolute uncertainties in the activation energies are in the 6 kJ/mol range. Because Gaussian calculations for small molecules have an uncertainty also in this range, the virtually exact agreement may be coincidental. The present shock tube results are derived on the basis of a second law analysis. Much more accurate results can be deduced on the basis of a third law analysis. This requires rate constants for the combination of hydroxyethyl radicals. The very accurate and generally accepted results for hydrocarbon radicals from these shock tube experiments were based on such analysis. Finally we note that the A-factor is in the expected 10^{16} s^{-1} range characteristic of the cleavage of C–C bonds. However, in this case the A-factor is in the low end of the usual range and is illustrative of

the problems mentioned earlier on the results of a second law analysis that is dependent on the slope of the measurements.

It is interesting to make the same type of comparison for the earlier study that deals with 1-butanol decomposition. In this case the bond dissociation energy is 417 kJ/mol or slightly lower than the value calculated by Curtiss et al. However, the experimental values are all greatly at variance. It is clear that if the bond dissociation energy is directly related to a particular rate constant careful attention must be paid to the accuracy requirements in the use of that particular value in a specific application.

CONCLUDING REMARKS

Dilute concentrations of 2-butanol have been decomposed in a single pulse shock tube. The experimental observations show

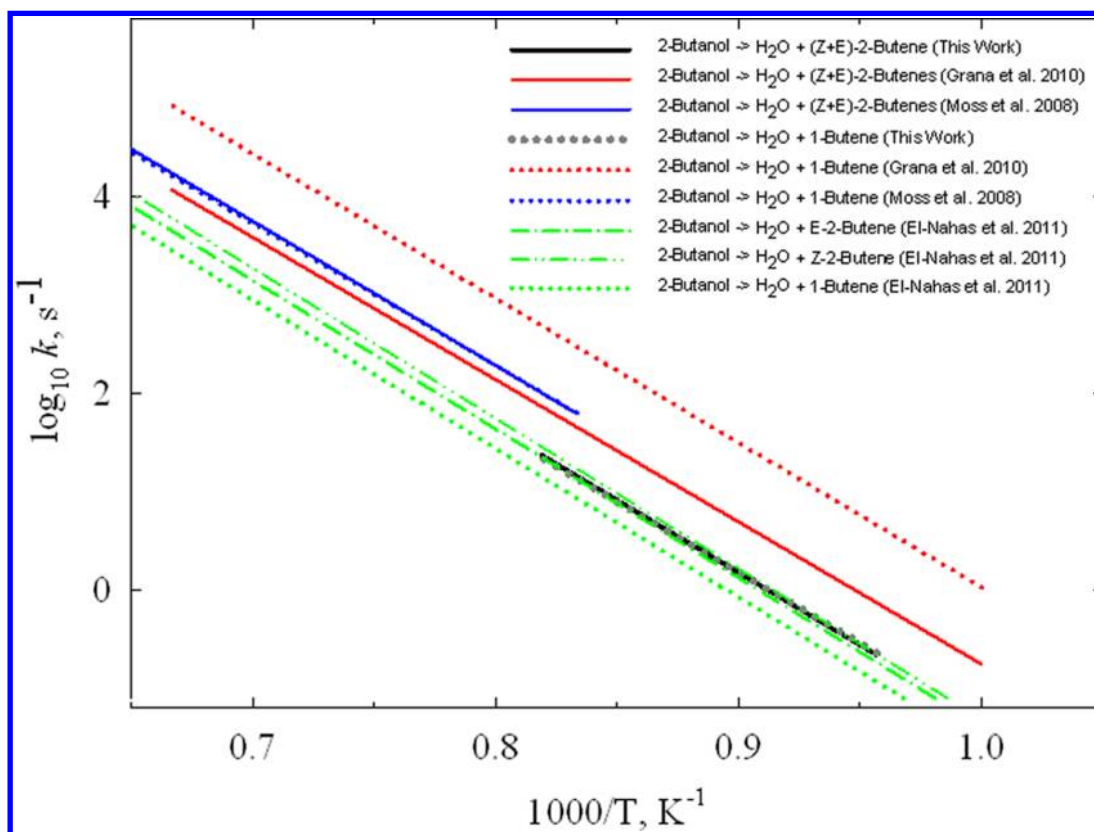


Figure 7. Arrhenius plot for the reaction of alcohol \rightarrow H_2O + olefin (per H atom β to OH).

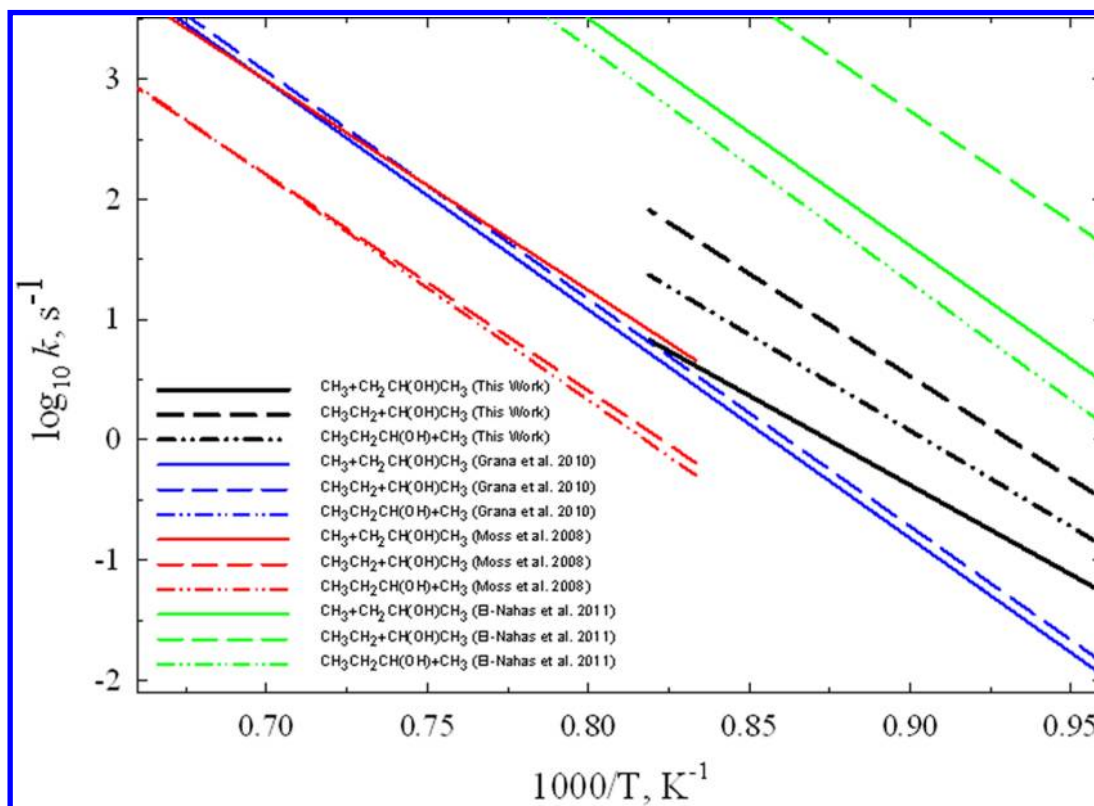


Figure 8. Rate constants for 2-butanol decomposition pertaining unimolecular initiation reactions; comparison of this work with other shock-tube and modeling studies.

that 2-butanol decomposes via C–C fission and concerted water elimination. The product distribution led to the

determination of temperature dependent rate expressions for these reaction channels. Rate expressions for these four

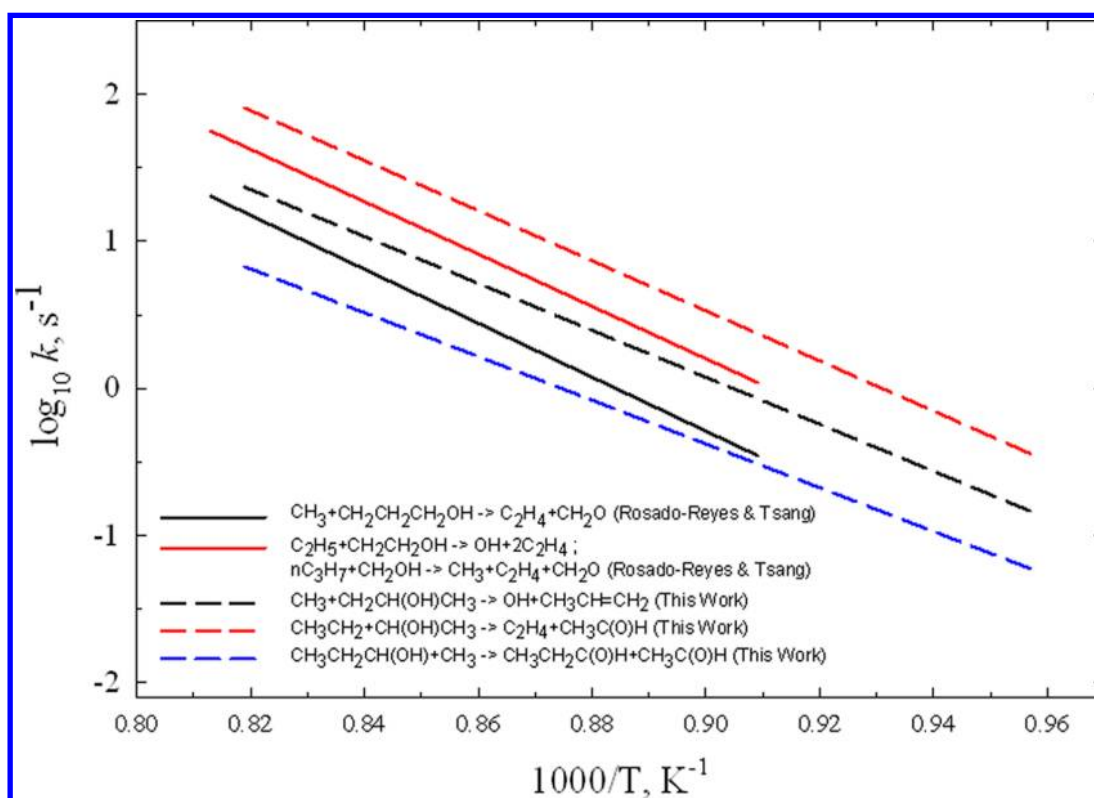


Figure 9. Comparison of rate constants for *n*-butanol (solid lines) and 2-butanol (dashed lines) decomposition pertaining unimolecular initiation reactions, derived from shock tube experiments.

channels have been determined from the experimental yields of ethylene and the three different butenes. Comparisons are made with literature values from experiments, theory and rate rules. The chemical kinetic information derived in this study provides critical experimental measurements, with a realistic estimate of the uncertainties, for comparison to simulations of the combustion chemistry of alcohols. It may have implications regarding the use of simulations in general for the prediction of combustion properties.

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Notes

The authors declare no competing financial interest.

REFERENCES

- (1) Lewis, D.; Keil, M.; Sarr, M. J. *Am. Chem. Soc.* **1974**, *96*, 4398–4404.
- (2) Tsang, W. *Int. J. Chem. Kinet.* **1976**, *8*, 173–192.
- (3) Moss, J. T.; Berkowitz, A. M.; Oehlschlaeger, M. A.; Biet, J.; Warth, V.; Glaude, P.-A.; Battin-Leclerc, F. *J. Phys. Chem. A* **2008**, *112*, 10843–10855.
- (4) Dagaut, P.; Togbé, C. *Fuel* **2008**, *87*, 3313–3321.
- (5) Grana, R.; Frassoldati, A.; Faravelli, T.; Niemann, U.; Ranzi, E.; Seiser, R.; Cattolica, R.; Seshadri, K. *Combust. Flame* **2010**, *157*, 2137–2154.
- (6) El-Nahas, A. M.; Mangood, A. H.; Takeuchi, H.; Taketsugu, T. *J. Phys. Chem. A* **2011**, *115*, 2837–2846.
- (7) Rosado-Reyes, C. M.; Tsang, W. *J. Phys. Chem. A* **2012**, in press (DOI: 10.1021/jp305120h).
- (8) Tsang, W. In *Energetics of Stable Molecules and Reactive Intermediates*; Piedade, M. E. M., Ed.; Kluwer Academic Publishers: London, 1999; Vol. 535, p 323.
- (9) Tsang, W.; McGivern, S.; Manion, J. A. *Proc. Combust. Inst.* **2009**, *32*, 131–138.
- (10) Wang, H.; Dames, E.; Sirjean, B.; Sheen, D. A.; Tangko, R.; Violi, A.; Lai, J. Y. W.; Egolfopoulos, F. N.; Davidson, D. F.; Hanson, R. K.; Bowman, C. T.; Law, C. K.; Tsang, W.; Cernansky, N. P.; Miller, D. L.; Lindstedt, R. P. *JetSurF* version 2.0 ed., 2010.
- (11) Moc, J.; Simmie, J. M.; Curran, H. J. *J. Mol. Struct.* **2009**, *928*, 149–157.
- (12) Maccoll, A.; Thomas, P. J. *Nature* **1955**, *176*, 392–393.
- (13) Disclaimer: Certain commercial materials and equipment are identified in this paper 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.
- (14) Tsang, W. *J. Chem. Phys.* **1965**, *42*, 1805–1809.
- (15) Alfassi, Z. B.; Golden, D. M. *J. Phys. Chem.* **1972**, *76*, 3314–3319.
- (16) Curtiss, L. A.; Lucas, D. J.; Pople, J. A. *J. Chem. Phys.* **1995**, *102*, 3292–3300.