Thermal Stability of Larger Carbonyl Compounds: 2-Methylbutyraldehyde

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ABSTRACT: We have decomposed 2-methylbutyraldehye in single pulse shock tube experiments, at temperatures between 1075 K to 1250 K and pressures of 1.5 and 6 atm. Five reaction channels have been identified from the unimolecular products that have been detected. The products involve C–C bond cleavage together with a retro-ene reaction. Particularly remarkable is the detection of small amount of butane; the first time that an alkane has been detected in these high-temperature experiments. The formation of butane represents evidence of the roaming radical reaction or more generally the high-temperature radical disproportionation reaction. Ethylene is present in large yields, and this is traced to a 1,2 H-transfer reaction involving the highly exothermic transfer of a carbonyl hydrogen to an alkyl site. The results are consistent with earlier single pulse shock tube experiments on the 2-ketones. In particular, they confirm the earlier observation that substituting a methyl and hydrogen atom with a doubly bonded oxygen atom have very little effect on the rate constant of the adjoining C–C bond. The yields of ethylene are consistent with a very low value of the carbonyl resonance energy. © 2014 Wiley Periodicals, Inc. Int J Chem Kinet 46: 285–293, 2014

INTRODUCTION

This paper is a continuation of earlier studies on the quantitative details of the decomposition of larger organic compounds in the gas phase and in the absence of radical-induced processes. The aim is to determine the mechanism and rate expressions for these processes. Hitherto, we have studied alkanes, alkenes, alkynes, branched aromatics, alcohols, ketones, amines, and alkyl halides [1]. These decompose by various molecular and bond cleavage processes. The rate expressions for the latter are consistent with the bond energies of the C–C bond being broken and the *A* factors show lower values as the temperature increases [2]. A summary of relevant bond dissociation energies can be found in a review published over a decade ago [3] and it shows the differences with values that were generally used for many years [4]. While there has been little change in recent years, theoretical work has now furnished additional support [5] for smaller radicals at least. Thus for unsaturated hydrocarbons, there are processes involving six center transition states, usually termed the retro-ene reaction. In the case of alcohols, there are two channels, dehydration and C–C bond cleavage. We have recently established the rate rules for these processes [6,7]. In the case of the ketones, [8] we have found that C–C bond cleavage processes are the predominant decomposition mechanism with only a minor retro-ene decomposition channel. One would

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expect that the aldehydes will be a simple extension of these observations.

More recent studies on the so-called "roaming" reactions suggest that there may well be far richer chemistry [9,10]. This is due to the discovery of the reaction of methyl and formyl radicals, where the main reaction channel turns out to produce methane and carbon monoxide. Theoretical explanation of these results have been provided by Bowman and Shepler [9]. Sivaramakrishnan et al. [10] provided evidence for small contributions for this type of reaction for the decomposition of isobutane and neopentane. Although not acknowledged, the general issue is related to the discovery of disproportionation products during the combination of alkyl radicals at room temperature with much discussion regarding the nature of the transition state [11].

The presence of molecular products in thermal decompositions that are initiated by bond breaking is directly related to disproportionation reactions. Thus the failure to detect smaller alkanes from the decomposition of the larger alkanes from single pulse shock tube experiments would seem to rule out this possibility. In single pulse shock tube studies, methane cannot be used as a marker of the reaction since methyl radicals will always be converted to methane by reaction with a reaction scavenger. On the other hand, any larger alkyl radicals with an ethyl terminal will always decompose into an olefin due to the high temperatures, characteristic of single pulse shock tube experiments. There is very little question that smaller alkanes are more stable than the associated larger compounds. Hence any detection of such small alkanes except for methane and ethane is indicative of their direct formation and to some extent may be considered as evidence for their formation during their initial decomposition process.

The presence of molecular channels in the decomposition of hydrocarbons is of great importance in high-temperature processes because it will reduce the concentration of radicals that are formed. These radicals dictate the course of the chain branching. Combustion is of course the best example of this.

The subject of this study is 2-methylbutyraldehyde. From the previous study of ketones [8] predictions can be made on the various C–C bond cleavage reactions that can occur. A particularly interesting reaction is involving the breaking of the C–C bond next to the carbonyl group that will lead to the formation of a formyl and secondary butyl radical. If roaming occurs, an important product that will be formed is normal butane. This is of course analogous to the formation of methane and carbon monoxide from the combination of formyl and methyl radicals. We have previously studied the decomposition of 3,4-dimethylhexane [12]. The main reaction releases sec-butyl radical into the system. Beta bond scission releases propene and methyl radicals. A minor reaction channel releases H atoms and 2-butenes. In addition, the breaking of appropriate C–C bonds will yield radical products, except for methyl, that will readily decompose into appropriate olefins.

Another interesting issue involves the carbonyl resonance energy. The experimental studies on ketones have indicated that the carbonyl resonance energy is much smaller than the allylic resonance energy [4]. However, ab initio calculations indicate an equal or larger value than for allyl radicals [13]. Finally, we note that the carbonyl-H bond energy is much lower than that for hydrocarbons, with an actual magnitude on the order of 42 kJ/mol [3]. This discrepancy raises the question of possible contribution from 1-2 and 1-3 hydrogen transfer processes leading to the formation of a carbonyl-type radical that will subsequently release CO directly. It is quite clear that a number of interesting new elements are introduced by the addition of a formyl group to a hydrocarbon framework, and this study is carried out with the hope of obtaining insights into the nature of these processes.

Table I summarizes some past work on related systems, such as ketones, alkanes, and alkenes. Note the similarities and differences in the rate constants and expressions that involve the addition of a carbonyl system into the basic alkane framework. Such comparisons lead to very suggestive rate rules that are expected to be manifested in the course of the experiments. The two significant structural elements are the introduction of the oxygen atom and the double bond. It is interesting that the bond energy of a carbon-vinyl bond is enormously larger than the C–carbonyl bond being broken in these studies. In comparable olefins, the 48 kJ/mol resonance energy is so much larger than an ordinary C–C bond. Thus the overwhelming process is the breaking of the carbon allylic bond. The overall effect of substituting the doubly bonded oxygen atom for a methyl group and hydrogen atom is to lower the rate constant by 50%. This is a small change and is even more unexpected than in the case of the alcohols.

The experiments have been carried out in a single pulse shock tube under conditions that prevent radical-induced decomposition and isolate the initial unimolecular pyrolitic reaction for detailed study. This isolation is achieved by carrying out the shock tube studies under high dilution and in the presence of a chemical inhibitor that removes all active radicals from the reaction mixture and also allows the use of an internal standard for estimating the temperature behind the reflected shock wave. The chemical inhibitor utilized in this study is 1,3,5-trimethylbenzene

Table I Past Work on Rate Expressions Rate Constants (1150 K) for Reactions Analogous to the Reactions Studies in This Study Dealing with 2-Methylbutyraldehyde

Reaction	Rate Expression (s^{-1})	Rate Constant (s^{-1}) (1150 K)
3-Methylpentanon-2 → $CH_3CO + s\text{-}C_4H_9$ [8]	$10^{16.4}\exp(-38{,}300\ K/T)$	35.9
5-Methylhexanone-2 → $CH_3COCH_2 + i\text{-}C_4H_9$ [8]	$10^{16.6}\exp(-40{,}600\ K/T)$	18.6
5-Methylhexanone-2 → $CH_3COCH_3 + i\text{-}C_4H_8$ [8]	$10^{12.56}\exp(-31{,}600\ K/T)$	4.2
Hexanone-2 → $CH_3COCH_3 + C_3H_6$ [8]	$10^{13.28}\exp(-32{,}400\ K/T)$	1.1
3-Methylpentane → $CH_3CH_2 + s\text{-}C_4H_9$ [12]	$10^{16.7}\exp(-40{,}000\ K/T)$	39.1/2
2,3-Dimethylpentane → $(CH_3)_2CH + s\text{-}C_4H_9$ [12]	$10^{16.1}\exp(-38{,}100\ K/T)$	53.1
2-Methylbutane → $CH_3 + s\text{-}C_4H_9$ [12]	$10^{16.4}\exp(-42{,}100\ K/T)$	3.15/2
1-Hexene → allyl + *n*-propyl [14]	$10^{15.9}\exp(-35{,}600\ K/T)$	288
1-Hexene → 2 propene [14]	$10^{12.64}\exp(-28{,}900\ K/T)$	48.8

The rate constants are divided by 2 to take into account the reactions where there are two pathways.

(135TMB). Radical attack on 135TMB leads to the formation of the benzyl-type reaction that is unreactive under the present environment.

EXPERIMENTAL*

The basic procedures used in carrying out the comparative rate single pulse shock tube experiments have been discussed in detail in earlier studies [1,15,16]. The reaction mixtures used in these studies are 500 μL/L 2-methylbutyraldehyde (target species; $\geq$95%; Sigma-Aldrich, St. Louis, MO, USA), 200 μL/L of cyclohexene (internal standard; 99+%; Sigma-Aldrich), and 10,000 μL/L 135TMB (chemical inhibitor; 99%; Sigma-Aldrich) at 1.5 and 6 atm of argon (99.999%; Paxair, Danbury, CT, USA) pressure. Some experiments were also carried out without cyclohexene to verify the product distribution. The cyclohexene decompose via the reverse Diels–Alder reaction is characterized by the rate expression [16]

$$\begin{aligned} &k(\text{cyclohexene} \rightarrow \text{ethylene} + 1,3\text{ butadiene}) \\ &\quad = 1.4 \times 10^{15}\exp(-33{,}500\ \text{K/T})\ \text{s}^{-1} \end{aligned}$$

We can then extract the reaction temperature from the relation

$$\frac{1}{T} = \frac{-R}{E_a}\ln\left(\frac{-1}{At}\ln\left(1 - \frac{[1,3-\text{butadiene}]}{[\text{cyclohexene}]_i}\right)\right)$$

where the rate constant is defined as $kt = -\ln(1-([1,3\text{-butadiene}]/[\text{cyclohexene}]_i)) = A\exp(-E_a/RT)$ and t is the residence time of approximately 500 μs. Note that this is the same residence time that is used in defining the rate constant for the decomposition process involving the target molecule 2-methylbutyraldehyde. Since the target and standard molecules are in the same sample, they must also experience the same temperature. There is thus large-scale canceling of the usual kinetic uncertainties. Hence the data precision is very high and the scatter is only from the gas chromatographic measurements. The addition of the radical inhibitor removes mechanistic artifacts from affecting the rate expressions that are obtained. In addition, since both target and standard compounds must have suffered the same temperature and time resolution, a drastic reduction of the experimental scatter is achieved.

Postshock samples are immediately extracted from the shock tube through the sampling port into the vacuum valve and loop sampling system, consisting of two valves and loop samplers, where the undiluted gas sample is compressed to 1 atm of pressure, separated into two loop volumes of 1 mL each, and then injected into two gas chromatographic columns for species separation. The gas chromatography system (Agilent Technologies, Santa Clara, CA, USA; model 6890N) was equipped with twin flame ionization detectors (FID) and an Agilent Technologies 5973 inert mass selective (MS) detector for mass spectral analyses. C_4 and larger compounds are separated in a J&W Scientific 30 m × 0.53 mm i.d. DB-1 fused silica (100% dimethylpolysiloxane) column. The eluting fraction from DB-1 is split for simultaneous FID and MS analyses. Lighter compounds are separated efficiently in a Restek 30 m × 0.53 mm i.d. RT-Alumina (aluminum oxide porous layer) capillary column. Peak

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*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.

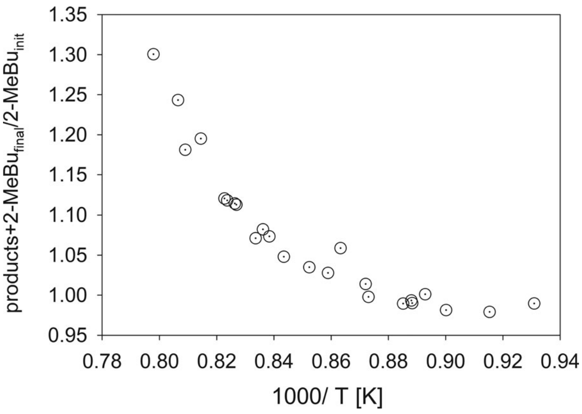

Figure 1 Molar product fractions formed from the thermal decomposition of 2-methylbutyraldehyde.

areas from FID are determined using Agilent Technologies ChemStation software and converted to molar quantities based on experimentally determined response factors. Retention times and molar FID responses of all starting substrates and products were determined from standard samples. The *n*-alkanes and *n*-alkenes were calibrated with commercial samples (GRACE, Inc.) containing 100 μL/L of each component. For other components, calibrations were made from measured vapor pressures of degassed components to prepare in-house mixtures. Experimental response factors were determined for ethylene, propene, *n*-butane, 1-butene, 2-butene, 1,3-butadiene, and cyclohexene. The estimated standard uncertainty (1σ) in the analysis of these components is no more than 3%. The FID sensitivities for acrolein, propionaldehyde, and 2-methylbutyraldehyde were obtained from previously measured FID relative molar response factors [17].

RESULTS

The detected products from 2-methylbutyraldehyde decomposition are ethylene, propene, acrolein, propionaldehyde, *n*-butane, 1-butene, and 2-butene. Ethylene is the major product, and its yield is particularly prominent as the temperature is increased. Carbon monoxide and formaldehyde are stable products that cannot be detected with our analytical system. Large quantities of methane and ethane are present. These can be formed from methyl radicals in the system that abstract H atoms from the scavenger and their recombination and will not be used in the present analysis. Considerable amounts of the butene isomers (1-butene and 2-butene) are also present. They appear at a very low extent of decomposition. We attribute this to the rapid decomposition of traces of a labile unknown impurity with concentrations of less than 1 or 2%. Note that by studying reactions under high inhibition conditions, this process cannot contribute to the decomposition mechanism. The large yields of butenes prevent us from determining the contributions of these compounds from the sec-butyl radicals and were not considered for product analysis. We have previously found that they contribute about 10% to the decomposition of the secondary butyl radicals where the main process is beta bond scission to form propene. However, even ignoring the butenes formed in this manner did not remove the small upward shift of the ethylene and downward shift of the propene yields (see Fig. 2 below). We have accordingly only analyzed quantitatively the results from 1136 K upward, purely arbitrary.

Typical results at various extents of decomposition are presented in Fig. 1 in terms of the total product yield and placed on a more quantitative basis for specific products in Fig. 2. At high extents of decompositions on a purely molar basis, more products are formed compared with the quantities of 2-methylbutyraldehyde that has disappeared. Obviously, there has been some double counting; the breakup of 2-methylbutyraldehyde leads to the presence of more than one detectable fragment. Thus, for example, the detection of propionaldehyde suggests the simultaneous formation of ethylene via a retro-ene reaction.

As seen in Fig. 3, there are of course multiple channels that can lead to the formation of more than one stable fragment. One of these stable fragments is ethylene; it is the product in the highest concentration. Consider the situation when an ethyl radical is formed upon the cleavage of the appropriate C-ethyl bond. The associated product to this cleavage is the propionaldehyde-2 radical. Beta bond scission will yield acrolein, and this was indeed detected. Thus acrolein and ethylene can form from the same 2-methylbutyraldehyde. However, the acrolein to ethylene ratio is not equal to unity. The retro-ene reaction will provide equal amounts of ethylene and propionaldehyde. Here again, the excess ethylene cannot be accounted for.

There remains the possibility of a 1,2-hydrogen shift involving the hydrogen atom adjacent to the carbonyl group. There has been no experimental observation of this process. Theory has shown that for alkyl radicals, 1,2-hydrogen shifts will require an activation energy of nearly 170 kJ/mol [18]. This is substantially higher than the usual competitive beta bond scission reaction involving C–C and C–H bond scission [3]. However, for alkyl radicals this is essentially a thermoneutral reaction. In contrast, the binding energy of the carbonyl C–H bond is extraordinarily small, of the order of 370 kJ/mol. This is much smaller than that of the

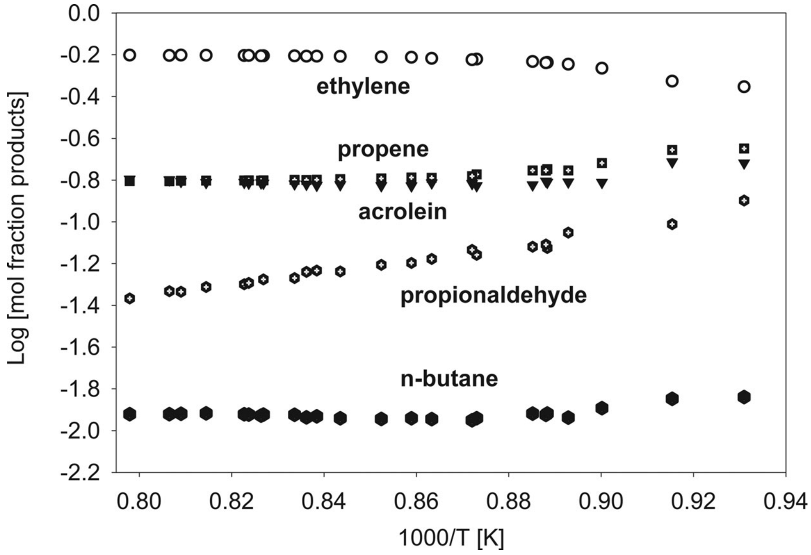

Figure 2 Fractional yields of product from 2-methylbutyraldehyde decomposition.

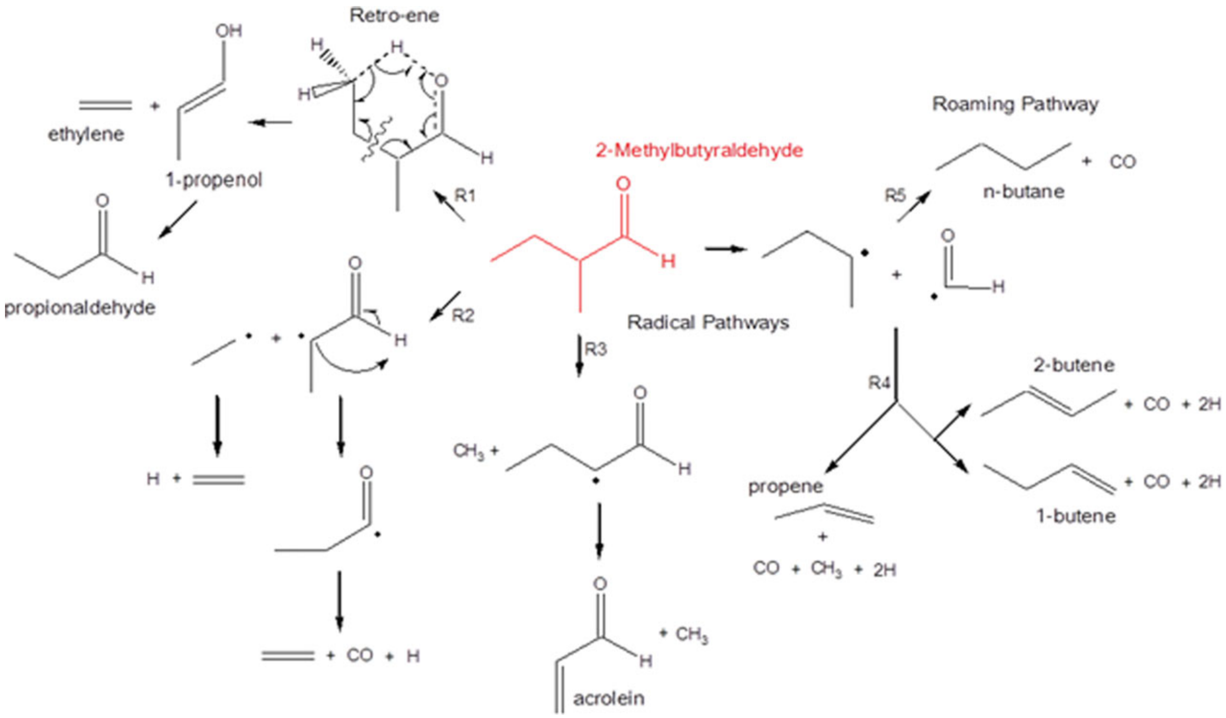

Figure 3 Mechanism for the decomposition of 2-methylbutyraldehyde.

secondary C–H bond of the order of 410 kJ/mol. If this difference is directly transferable to the activation energies of H atom transfer, then it will bring the subsequent radical destruction process into the same range of values as beta C–H and C–C cleavages. Note that the subsequent decomposition of the carbonyl compound has an extremely small barrier of less than 55 kJ/mol [3]. Once the carbonyl radical is formed, the subsequent decomposition reaction can be considered to be instantaneous. Two ethylene molecules are formed for every ethyl-propionaldehyde-2 bond that is broken, and this will in fact bring about a satisfactory mass balance. Note that the data in Fig. 1 become insensitive to these effects at a low extent of reaction. In the case of a very small extent of reaction, the mass balance considerations discussed here will be inapplicable.

Aside from C–C bond cleavage yielding an ethyl radical, the ejection of a methyl grouping will leave a butyraldehyde-2 radical. Beta bond cleavage of a C–C bond will lead to acrolein. The latter is a more likely process than the ejection of a C–H bond from the propionaldehyde-2 radical since there is an activation barrier difference of at least 25 kJ/mol. This process will only lead to acrolein formation and therefore will not help in reducing the excess products that have been detected. Thus the ejection of ethyl and methyl can both lead to acrolein formation and the issue is then the partitioning of the acrolein between the sources. However, there are not sufficient data to decide on the proper data partitioning and analysis. For the present purposes, it will be assumed that ethyl ejection will lead to another ethylene being formed as a consequence of 1,2 hydrogen shift and methyl ejection is the sole source of acrolein. This assumption leads to an ethyl and methyl rate constants for ejection of a factor of two difference and appears to be somewhat small based on hydrocarbon data. It exactly balances the measured mole fractions formed and destroyed. The partitioning of the methyl and ethyl ejection channels will lead to the possibility of some untabulated channels.

The data in Fig. 2 show the fractional yield for the particular product channel of interest. The results at lower temperatures depart from linearity, showing a smaller ethylene yield and larger yields of the other products. A simple explanation is that at the lower temperatures the two ethylenes are no longer produced following the cleavage of the ethyl-propionaldehyde-2 bond. The general mechanism is shown in Fig. 3.

The most interesting product is undoubtedly *n*-butane. This is the first time that we have detected a larger alkane in all the studies carried out in our single pulse shock tube experiments. *n*-Butane is indicative of a direct molecular reaction leading to the formation of carbon monoxide. Nevertheless, it is present in much smaller quantities than the olefins. Because of the isomeric butenes that are formed at the lower temperature we have assumed that for every propene molecule that is detected, approximately a further 10% of the sec–butyl radical is formed from the hydrogen-ejection channel, a ratio that we have found earlier when a compound such as 3,4-dimethylhexane is decomposed in single pulse shock tube experiments [12].

Figure 4 contains Arrhenius plots of rate constants as a function of temperature. We follow the standard procedure for treating multichannel unimolecular decomposition processes. Specifically, we define

$$k(\text{total}) = k(\text{R1}) + k(\text{R2}) + k(\text{R3}) + k(\text{R4}) + k(\text{R5})$$

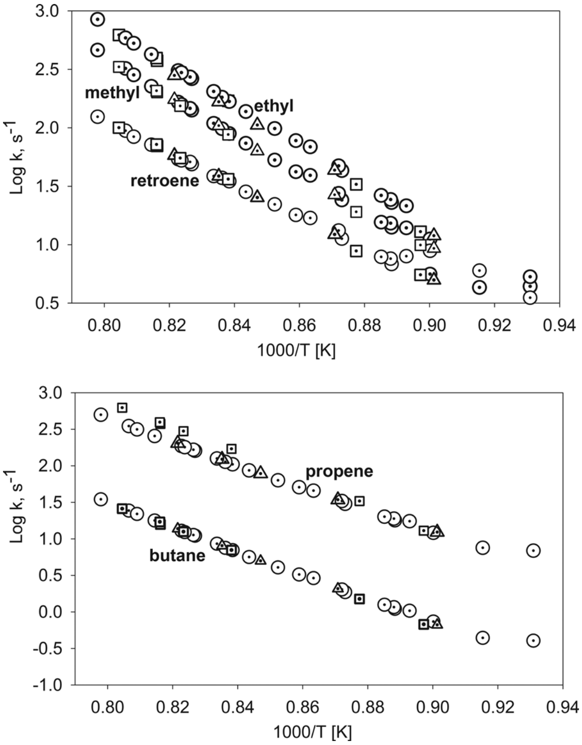

Figure 4 Rate constants as a function of temperature for the processes of interest. Ethyl refers to the process that yields ethylene (reaction (2)). Methyl deals with reactions that yield acrolein (reaction (3)). The retro-ene reaction involves direct formation of propionaldehyde (reaction (1)). The propene is derived from the sec-butyl radical (reaction (4)), and butane is the roaming reaction that accompanies the bond breaking (reaction (5)). Circles are reactions at 3 atm, triangles are for reactions at 6 atm, and squares are for processes at 1.5 atm. Rate measurements are arbitrarily truncated at 1180 K due to reasons discussed in the text. Rate measurements are truncated at 1135 K due to reasons discussed in the text.

where

$$k(\text{R1}) = [\text{propionaldehyde}]_{\text{retroene reaction}}$$

$$k(\text{R2}) = [\text{ethylene} - \text{propionaldehyde}]/2$$

$$k(\text{R3}) = [\text{acrolein}]$$

$$k(\text{R4}) = [\text{s} - \text{butyl} + \text{formyl}] = 1.1 \times [\text{propene}]$$

where we have multiplied the propene yield by the factor of 1.1 to take into account the butane isomers formed during the course of s-butyl radical decomposition as determined from earlier studies:

$$k(\text{R5}) = [n - \text{butane}]$$

Table II Summary Data on the Various Processes Involved in the Decomposition of 2-Methylbutyraldehyde in Single Pulse Shock Tube Experiments

Reaction	Rate Expression (s^{-1})	Rate Constant (s^{-1}) (1150 K)
R1: 2-me-butyraldehyde → ethylene + propionaldehyde	$10^{13.01 \pm 0.14} \exp(-31{,}540 \pm 200\ K/T)$	12.3 ± 0.04
R2: 2-me-butyraldehyde → ethyl + *n*-propionaldehyde-2	$10^{16.35 \pm 0.11} \exp(-38{,}830 \pm 310\ K/T)$	49.9 ± 2
R3: 2-me-butyraldehyde → methyl + *n*-butyraldehyde-2	$10^{15.85 \pm 0.15} \exp(-38{,}500 \pm 300\ K/T)$	20.5 ± 1
R4; 2-me-butyraldehyde → s-butyl + formyl	$10^{15.32 \pm 0.1} \exp(-36{,}540 \pm 300\ K/T)$	34.5 ± 1.5
R5: 2-me-butyraldehyde → *n*-butane + CO	$10^{14.83 \pm 0.08} \exp(-38{,}400 \pm 230\ K/T)$	2.39 ± 0.06

This furnishes a basis for comparison with the data summarized in Table I.

k(R5) is the roaming reaction and should be included with the rate constant for s-butyl radical formation as a total rate constant for the breaking of the secondary butyl–formyl bond.

From the experimental data, we obtain

$$\mathrm{k(total)} = -\ln(1 - [\mathrm{totalproducts}/\mathrm{initial\ 2-methylbutyraldehyde}])/\mathrm{t}$$

where *t* is the residence time of 500 μs and the total products include ethylene, propionaldehyde, acrolein, propene, and *n*-butane.

The individual rate constants can then be obtained from the relation

$$\mathrm{k(process)_j/k(total)} = \mathrm{concentration_j}/\mathrm{total\ product\ concentration},$$

where the subscript *j* refers to the individual processes described above.

The Arrhenius plots of the five individual processes are included in Fig. 4. The reader is reminded that the acrolein yield is assigned to the formation of methyl radical and is probably an overestimate because methyl will also be released during the formation of propene. Most of the above discussion center about the assumptions that must be made with regard to the ethylene that is formed. They thus impinge on the reactions involved in the ejection of methyl and ethyl radicals. They do not necessarily impinge on the processes that deal with the breaking of the sec–butyl–formyl bond or the retro-ene reaction that leads to the direct formation of propionaldehyde and ethylene. However, because of the apparent drop in formation of ethylene and the corresponding increase in the relative mole fractions of the other products, the rate expressions may be effected.

The rate expressions that we have obtained are given in Table II. We have used the same format as in Table I to facilitate comparisons. The uncertainties included are the result of the least square analysis and are extremely small directly due to the internal standard technique. Overall, they lead to absolute uncertainties of approximately a factor of 2 in the *A* factor and 6 kJ/mol in the activation energy. However, practically all uncertainties in rate constants and expressions arise from mechanistic ambiguities. The present discussion is fully indicative of these problems.

DISCUSSION

A large number of products are formed during 2-methylbutyraldehyde decomposition in a single pulse shock tube. The analysis of the results is helped by the detection of smaller aldehydes. Except for the direct formation of butane, the rate expressions and constants obtained here can be directly compared with values in Table I. Specifically, there does not appear to be any drastic change in the rate expressions or constants between the aldehydes and the ketones.

There is somewhat larger spread of *A* factors than that in the data included in Table I. For the bond cleavage reactions, this is undoubtedly due to the formation of the butenes at a low extent of conversions that we have ignored in the treatment of the bond cleavage reactions. More support for this assumption is furnished by the analogous heat of formation for the formyl radical described below. It is of course well known that rate constants are more accurately determined than their temperature dependence (slope). More valid direct comparisons can be made in terms of the rate constants at a common temperature. These are the actual experimental values that are directly measured. This is equivalent to comparing equilibrium constants as opposed to the thermodynamic quantities that may be inferred. However, even on this finer basis, the general trends are very similar. Unfortunately, except for the C–C bond cleavages of the formyl-s-butyl and acetyl-butyl bonds, exact comparisons cannot be made. The rate constant for formyl and acetyl substitution leads to values that are virtually unchanged. Apparently, methyl substitution has minimal effects on rate constants of carbonyl compounds. This is somewhat equivalent in going from an ethyl to isopropyl situation in the alkanes where the rate constants change only minimally. Comparison of the carbonyl compounds to the alkanes indicates the same minimal effects. In the case of ketones, there is a decrease of a factor of 1.5 in rate constants which is not observed for the aldehyde. It is indeed somewhat surprising that such drastic structural change such as going from a methylene to a carbonyl structure should lead to such small changes. There appears to be a very simple rate rule in going from alkanes to carbonyl compounds for the bonds adjacent to the carbonyl compound. The retroene reactions show larger effect with the rate constants for carbonyl compounds being considerably smaller. Intuitively, this is consistent with smaller resonance energy.

For the decomposition of the sec–butyl–acetyl (Table I) and sec–butyl–formyl (Table II) bonds, there appears to be an order of magnitude difference in the *A* factor and a 13 kJ/mol difference in the activation energies. However, the rate constants differ by less than a factor of 1.5. The question naturally arises whether this is due to a compensation effect arising from the problems described earlier for measuring the rate constant as a function of temperature. For this purpose, we can use our results to determine the heat of formation of the formyl radical and use this as a check of the derived rate expression. Assuming that the reverse combination reaction between formyl and the s-butyl radical has no activation energy, then

$$\begin{aligned}\Delta H &= \Delta E + RT = 305 + 9.6 \\ &= 314.6\,\text{kJ/mol at 1150 K}\end{aligned}$$

From the heat of formation of 2-methylbutyraldehyde of −257.3 kJ/mol [19] at 1150 K, a heat of formation of the secondary butyl radical of 39.5 kJ/mol [5] at 1150 K, and the bond dissociation energy (BDE) (s-butyl-H) = 414.2 kJ/mol [20], we find the heat of formation at 1150 K for the formyl radical to be 17.8 kJ/mol. Correcting to room temperature, this leads to the value of 23 kJ/mol. The well-established heat of formation of formyl radical is 42 kJ/mol. Our results deviates by 19 kJ/mol, and if this arises from an error in the slope of the determination of the activation energy the results would require raising the *A* factor to 1.6 × 10 [15]. This adjustment will place our formyl radical heat of formation well within the range of values for the ketones and alkanes tabulated in Table I and numerous other studies on alkane decomposition. There is of course no reason that the *A* factors for so many different systems should be very close to each other. Indeed, the formyl group probably has characteristics of a diatomic species that would be expected to have smaller *A* factors. Apparently, the magnitude for such effects is not large. Indeed, in the alkenes it is possible to recognize the effect of vinyl substitution and consequently allylic resonance by roughly a factor of three smaller *A* factors. There is no such evidence in the case of the carbonyl compound.

The presence of normal butane provides evidence for the presence of a roaming channel in the decomposition of a larger polyatomic molecule. It is in such a small amount that for practical purposes, it will not make much of a contribution to a high-temperature system. Note that we do not report on the other possible roaming product, the abstraction of hydrogen atom from the s–butyl radical by the formyl radical. We do note that at the highest temperatures the butene isomers are slightly in excess (factor of 2) than expected, roughly 10% of the propene yield in other s-butyl systems. This cannot be a major channel. In the present analysis, the s-butyl-formyl reaction channel has been treated at the sole bond-breaking process. Presumably, the "roaming" reactions should be included. It is, however, such a small component and thus will not affect the conclusions drawn above.

Finally, we note that although there does not appear to be large contributions for a carbonyl resonance energy, our results do not rule out a small contribution of the order of 10 kJ/mol. This will probably be manifested in a smaller activation energy for the relevant C–C bond.

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