

SINGLE PULSE SHOCK TUBE STUDIES ON
THE STABILITY OF 1-PHENYLBUTENE-2

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ABSTRACT

1-Phenylbutene-2(1-PHB-2) has been decomposed in single pulse shock tube experiments. Acetylene formation is used as a measure of the rate of cleavage of the benzyl-vinyl C-C bond. The rate expression for this reaction has been found to be

$$k(1\text{-PHB-2} \rightarrow \text{benzyl} + \text{propenyl}) = 2.4 \times 10^{16} \text{ Exp}(-43780/T) / \text{s.}$$

The A-factor for this process is unexpectedly large. It may be indicative of a larger than usual combination rate constant for vinyl radicals. Possible sources of experimental errors are considered. Our results are consistent with a bond dissociation energy for the primary vinyl C-H bond in propylene of 475 ± 10 kJ/mol.

INTRODUCTION

This paper is concerned with the strength of the primary vinyl C-H bond in propylene. The present results should provide additional information on the energy of the vinyl C-H bond in ethylene. Within the past year there have been values ranging from 435 to 495 kJ/mol^{1,2}. Any effect from methyl substitution will be far smaller than the spread of such numbers. The importance of the this quantity is due to the evidence³ that vinyl radicals are key reactive intermediates for soot formation. Unfortunately, there is at present almost no rate data on vinyl radical reactions and the uncertainty with regard to its heat of formation prevents even the most rudimentary efforts at estimation.

The experiments are carried out in a heated single pulse shock tube⁴. Our target molecule is 1-phenyl butene-2 (1-PHB-2). The choice of this molecule is dictated by the weakening of the vinyl C-C bond by benzyl resonance and the decreased stability of the propenyl radical compared to that of the vinyl radical itself (had we chosen to work with allylbenzene). The former lowers the rate constant to a range which is more convenient for our purposes. Nevertheless, the rate constants are still very much smaller than those for alkane and alkene decomposition that we have hitherto studied. This creates certain problems. The existence of a unique reaction product, acetylene, from the decomposition of the propenyl radical, should reduce complications.

The key factors in obtaining high accuracy results from single pulse shock tube work are the great simplifications in the reaction mechanism and the use of an internal standard reaction to calibrate for the conditions in the experiments. The general methodology has been successfully used to give a complete picture of the decomposition of many organic compounds⁵.

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There have been no previous studies on 1-PHB-2 decomposition. In Figure I(1), we outline a number of possible competitive unimolecular decomposition processes. From published bond energies one expects that they will be close to that for the vinyl-benzyl bond⁶. Unfortunately, these decomposition channels do not lead to unique products and it will not be possible to obtain accurate information on the rate constants for these reactions. This also makes it important to work at extents of conversion.

EXPERIMENTAL

The experiments are carried out in a heated single pulse shock tube maintained at 110 °C. All of the gas sampling systems are maintained at temperatures close to or above this value. It is thus possible to work with very low volatility substances. Analysis of the products was by gas chromatography using a 30 meter polydimethylsiloxane capillary column for all substances with carbon numbers 5 or higher. For the light hydrocarbons we use a dinonylphthalate coated silica column. This column eluted acetylene between propylene and isobutene. Unfortunately, the retention time of allene also fell in this position. From separate experiments we determined that our yields of allene was uniformly of the order of 4% of the acetylene yield. The 1-PHB-2 from K & K⁷. Gas chromatographic analysis indicated that it is mostly the trans compound with about 3% cis. There are also a number of other impurities. These included n-butylbenzene and s-butyl benzene. In these molecules, the normal C-C bonds are weakened by benzyl resonance. Since these are much more labile than vinyl C-C bonds, we observe under all conditions large quantities of their dissociation products. However under our conditions it is not possible to form acetylene from these starting materials.

In Figure I we enumerate the most likely decomposition modes of 1-PHB-2. Note that for methyl or larger alkyl radicals addition will be reversed, while the abstraction products will be the same as that for hydrogen atoms. The key conclusion from an examination of these possibilities is that under conditions of small extent of decomposition of the parent compound there is no channel that can lead to acetylene formation except through the sequence of reaction initiated by the cleavage of the propenyl-benzyl bond, followed by beta elimination of the methyl group.

Our concern with these factors arises from the high stability of the 1-phenylbutene-2 which prevents us from carrying out our experiments under conditions of enormous excesses of scavenger (100 to 1000 to 1). Indeed, a scavenger such as toluene will have rates of decomposition less than an order of magnitude slower. With a 100 to 1 ratio the scavenger will be producing more radicals than our test compound and will then have the capability of inducing decomposition. With this in mind, our highest scavenger 1,2,4-trimethylbenzene (1,2,4-TMB) to 1-PHB-2 ratio was 8 to 1. This appeared to be sufficient since our results with a 2 to 1 ratio are within experimental error the same as that at 8 to 1. The composition of the mixtures used and the range of conditions are summarized in Figure II.

The internal standard used in these studies is the reverse Diels Alder decomposition of 1-methylcyclohexene (1-MCH). We have previously established⁸ its rate expression for decomposition into 2-methyl-butadiene-1,3(isoprene) and ethylene as

$$k(1\text{-MCH} \rightarrow \text{isoprene} + \text{C}_2\text{H}_4) = 10^{15} \text{ Exp}(-33500/T)/s$$

This standard is used because isoprene is not a reaction product in 1-PHB-2 decomposition and it elutes from our capillary column in a region where there are no interfering peaks.

RESULTS

The distribution of products from the shock induced decomposition of 1-phenylbutene-2 in the presence and absence of the scavenger 1,2,4-TMB can be found in Table I. The important points to be noted are the changes in relative concentrations. We assume that acetylene is essentially a primary product and its concentration will not be effected by the absence and presence of the scavenger. Our results are in accord with the expectation that some of the reactive radicals will be removed by the 1,2,4-TMB. However, although there is a decrease in the yields of the lighter products (for example, propylene, butadiene) relative to that of acetylene as the amount of the inhibitor, 1,2,4-TMB is increased, we cannot be certain that we have been able to stop completely the radical induced decomposition. This is not unreasonable, since as noted earlier the thermal stability characteristics of 1-PHB-2 is not that much different than the inhibitor. Thus there approaches a point where our inhibitor will in fact be contributing to the pool of active radicals. It is interesting to note that the material balance with regard to 1-MCH decomposition improves with scavenger addition. Paralleling this is the decrease in the quantity of 1-PHB-2 destroyed when the scavenger is added. Clearly in the absence of the scavenger there are radical catalyzed decomposition channels.

For our purposes we concentrate on the acetylene from 1-PHB-2 decomposition and isoprene from 1-MCH decomposition. Figure II contains the comparative rate plots for the formation of acetylene from 1-PHB-2 decomposition and isoprene from 1-MCH decomposition. The rate constants are derived from the relation

$$\begin{aligned} \text{Log}(k(\text{acetylene})) &= \text{Log}((\text{acetylene})_f / (1\text{-PHB-2})_i) / t \\ \text{Log}(k(\text{isoprene})) &= \text{Log}(1 - (X * (\text{isoprene})_f / (1\text{-MCH})_i)) / X t \end{aligned}$$

where $X = 1 + ((\text{MCH})_i - (\text{MCH})_f - (\text{isoprene})_f) / ((\text{isoprene})_f)$ and takes into account the possibility that some of the 1-MCH $((\text{MCH})_i - (\text{MCH})_f - (\text{isoprene})_f)$ will be decomposed through radical attack. We have no means of determining how much isoprene is destroyed. Thus it is essential in the 1-MCH decomposition to obtain the best possible mass balance. This is attained when the scavenger is added. As will be seen below, in the absence of scavenger comparative rate results are different than in its presence. The relation for acetylene appearance assumes negligible 1-PHB-2 disappearance. From the data in Table I it can be seen that this is attained in the studies with the scavenger. We assume that the conversion of the trans to the cis form will not effect our results. An interesting aspect of the data in Table I is that we can extract rate constants for the trans \rightarrow cis isomerization of 1-PHB-2 as well and the decomposition of nbutyl- and sbutyl-benzene. In all three cases they fall in the expected range.

The comparative rate expressions relating the rate constant for acetylene and isoprene formation in 1-PHB-2 and 1-MCH decomposition are as follows;

$$\text{Log}(k(\text{acetylene})) = 1.308 + .014 \text{Log}(k(\text{isoprene})) - 3.030 + .034$$

(1% 1-PHB-2 and 200 ppm 1-MCH)

$$\text{Log}(k(\text{acetylene})) = 1.312 + .015 \text{Log}(k(\text{isoprene})) - 3.256 + .036$$

(1% 1,2,4 TMB; .5% 1-PHB-2 and 100ppm 1-MCH)

$$\text{Log}(k(\text{acetylene})) = 1.304 + .034 \text{Log}(k(\text{isoprene})) - 3.198 + .087$$

(2% 1,2,4 TMB; .25% 1-PHB-2 and 50 ppm 1-MCH)

Substituting into these relations the rate expression for the reverse Diels-Alder decomposition of 1-MCH given above, we obtain the following rate expression for acetylene formation in 1-PHB-2 decomposition $k(\text{acetylene}) = 3.8 \times 10^{16} \text{Exp}(-43800/T) / \text{s}$, $k(\text{acetylene}) = 2.6 \times 10^{16} \text{Exp}(-43900/T) / \text{s}$ and $k(\text{acetylene}) = 2.3 \times 10^{16} \text{Exp}(-43670/T) / \text{s}$ respectively.

It will be noted that the last two expressions are virtually identical, while the first rate expression is about 30 % larger. This is due to the contribution from the radical induced decomposition of 1-MCH and isoprene and is of the magnitude expected on the basis of our mass balance considerations. The agreement in the other two cases suggest that enough inhibitor has now been added so that the radical induced decomposition no longer poses a serious problem. The similarity in the activation is also interesting. It suggests that the contribution from the induced decomposition has very similar temperature dependence as the direct unimolecular decomposition. Our best rate expression for the breaking of the vinyl-benzyl bond is thus the average of our results in studies carried out in the presence of 1,2,4 TMB or

$$k(1\text{-PHB-2} \rightarrow \text{benzyl} + \text{propenyl}) = 2.4 \times 10^{16} \text{Exp}(-43780/T) / \text{s}$$

DISCUSSION

We will now use our rate expression for the breaking of the benzyl-vinyl bond to derive the bond energy of the primary C-H bond in propylene. From the usual assumption regarding the absence of temperature dependence for the reverse combination reaction, the relations are

$$\Delta H (\text{reaction}) = \Delta E (\text{activation Energy}) + RT$$

or $\Delta H = 409.6 \text{ kJ/mol}$ at 1150K. Since

$$\Delta H (\text{reaction}) = H_f(\text{benzyl}) + H_f(\text{propenyl}) - H_f(1\text{-PHB-2}) \text{ at } 1150\text{K}.$$

substituting the heat of formation of benzyl and 1-PHB-2 lead to $H_f(\text{propenyl}) = 269.5 \text{ kJ/mol}$. at 1150K. We have calculated the thermodynamic quantities of benzyl using the prescription of Benson and O'Neal⁹ and a value of 205 kJ/mol for the heat of formation at 300K. This is 6 kJ/mol higher than the number recommended by McMillen and Golden⁶, but is a value that we obtained some years ago on the basis of isobutyl benzene decomposition¹⁰. This leads to a heat of formation of 180.7 kJ/mol at 1150K. The heat of formation of 1-PHB-2 at 1150K is taken to be 80.3 kJ/mol and is based on the heat of formation of butylbenzene and an average value of 133 kJ/mol for the heat of dehydrogenation¹¹. Assuming that the heat capacity of propenyl is an average of that of propene and propyne leads to

$$\text{BDE}(\text{propene} \rightarrow \text{propenyl} + \text{H}) = 484 \pm 8 \text{ kJ/mol}$$

There have been no previous measurement of this bond dissociation energy. However, it should not be too far off from the value for ethylene. Our number is extraordinarily high and had it not been for the recent value of Shiromaru and coworkers would be the highest ever reported for such a bond. Most kinetic results appear to favor very low values.

The A-factor for acetylene formation, 2.4×10^{16} /s, is large in comparison to that for processes that involve the breaking of a benzyl-alkyl bond. In these cases A-factors are more in the range of one-half to one order of magnitude smaller. Our high number is reflected in the rate constant of the reverse recombination reaction. It is of interest to calculate the combination rate constant for benzyl attack on propenyl using our A-factor. From the estimated entropies we find that $\Delta S = 148 \text{ J/mol-K}$. Substitution into the relation,

$$A_f/A_b = \exp(-\Delta S/R)/eRT$$

leads to $A_b = k_b = 11 \times 10^{10} \text{ l/mol-s}$, with an uncertainty of a factor of 3. This is a large rate constant. It is much larger than the values for comparable processes involving alkyl radicals. Thus an interesting consequence of this study is that higher vinyl C-H bond energies not only lead to longer lifetimes for the decomposition of vinyl type radicals but predicts higher combination rates with other radicals.

In view of the unexpectedly larger recombination rates, it is important to consider possible sources of uncertainties in our measurements. The chief source of error is probably in the definition of the reaction mechanism. We have assumed that all the acetylene must be formed from the cleavage of the benzyl-vinyl C-C bond and that this will be followed by beta C-C bond cleavage. While we believe that these embody the main reactions, the fact that we are making a slope measurement means that small errors may lead to substantial errors. Probably the most serious is the assumption of beta C-C bond cleavage in propenyl decomposition and ignoring the possibility of a 1-3 bond shift leading to an allyl radical which will be fairly stable under our conditions. This assumption is based on the behavior of alkyl radicals. In the present case there may be some enhancement due to the much larger reaction exothermicity for the 1-3 shift (in excess of 60 kJ/mol). However, since we are dealing with a doubly bonded structure there will be an extra degree of strain in the transition state. Furthermore, in the decomposition of o-iodotoluene where we make the o-methylphenyl radical, which is structurally very similar to propenyl, there does not appear to be any evidence for such a shift. It should be noted that if such an effect is to make a contribution it will bias the results towards higher activation energies. The A-factor for 1-3 H-shift is smaller than that for beta C-C bond fission and this must be compensated for by a lower activation energy if this process is to make any contribution. Similarly, since the lowest energy path for acetylene formation in our system is the breaking of the benzyl-vinyl bond, then any other contribution will also lead to an increase in measured activation energy. On this basis we believe that to some extent our activation energy is an upper limit. A lower limit is set by the A-factor for the decomposition of a compound such as ethylbenzene or 4×10^{15} /s. This leads to a more "normal" A-factor $1.8 \times 10^{10} \text{ l/mol-s}$. Scaling our activation energy to obtain the same rate constant will lead to a value of 346 kJ/mol or a bond dissociation energy

of 465 kJ/mol. Taking the average of these two values we arrive at 475±10 kJ/mol as the most likely value. This is still a very large number. It is a reflection of the fact that our measured rate constants are much too small to be consistent with a low vinyl-H bond energy.

In a similar fashion it is interesting to consider the consequences of a bond dissociation energy in the 435 kJ/mol range. Assuming our rate constant to be correct, this will imply an A-factor of 3×10^{14} /s and a rate constant for combination of close to 10^9 l/mol-s. This strikes us as an extremely low and unlikely value. Even more unlikely is the highest reported value for the C-H bond energy in ethylene since this will lead to an A-factor of 2.5×10^{17} /s and a recombination rate of 11×10^{11} l/mol-s. or larger than collisional. On the other hand, a somewhat higher rate constant for vinyl radical combination is in line with increasing evidence for a very small disproportionation to combination rate constant ratio for vinyl radicals reacting with itself.

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Figure I: Important Steps in 1-Phenylbutene-2 Decomposition

1. Unimolecular Decomposition
 - a. C-H bond split $C_6H_5CH_2CH=CHCH_3 \rightarrow C_6H_5C\dot{C}H=CHCH_3 + H$
 $\rightarrow C_6H_5CH_2\dot{C}H=CHCH_2 + H$
 - b. C-C bond splits $C_6H_5CH_2CH=CHCH_3 \rightarrow C_6H_5 + \dot{C}H_2CH=CHCH_3$
 $\rightarrow C_6H_5CH_2 + \dot{C}H=CHCH_3$
2. Radical Attack (abstraction and addition)
 - a. $C_6H_5CH_2CH=CHCH_3 + R \rightarrow C_6H_5CHCH=CHCH_3 + RH$
 $\rightarrow C_6H_5CH_2CH=CH\dot{C}H_2 + RH$
 - b. $C_6H_5CH_2CH=CHCH_3 + H \rightarrow C_6H_6CH_2CH=CHCH_3$
 $\rightarrow C_6H_5CH_2CH_2\dot{C}HCH_3$
 $\rightarrow C_6H_5CH_2CHCH_2\dot{C}H_3$
3. Decomposition of Radicals

$CH_2\dot{C}H=CHCH_3 \rightarrow CH_2=CH\dot{C}H=CH_2$
 $C_6H_5CHCH=CHCH_3 \rightarrow C_6H_5\dot{C}H=CHCH=CH_2 + H$
 $C_6H_5CH_2CH=CHCH_2$
 (stabilized)
 $C_6H_6CH_2\dot{C}H=CHCH_3 \rightarrow C_6H_6 + CH_2\dot{C}H=CHCH_2$
 $C_6H_5CH_2CH_2\dot{C}HCH_3 \rightarrow C_6H_5CH_2 + C_3H_6$
 $C_6H_5CH_2CHCH_2\dot{C}H_3 \rightarrow C_6H_5CHCH=CH_3 + CH_3$
 $\dot{C}H=CHCH_3 \rightarrow \dot{C}H=CH + CH_3$
4. Decomposition Products from Impurities (nbutylbenzene, sbutylbenzene) leading to ethylene, styrene, methyl, methane, ethane, etc.

Figure II: Comparative Rate Studies on the Formation of Benzyl and Propenyl from 1-PHB-2 and 1-MCH Decomposition; 1% 1-PHB-2 and 200 ppm 1-MCH in Argon (□); 1% 1,2,4-TMB, .5% 1-PHB-2 and 100ppm 1-MCH in Argon (*); and 2% 1,2,4 TMB, .25% 1-PHB-2 and 50 ppm 1-MCH in Argon(●). Temperature, 1092-1221 K; Residence time 500 microseconds.; Pressure, 2.5-3.5 atms.

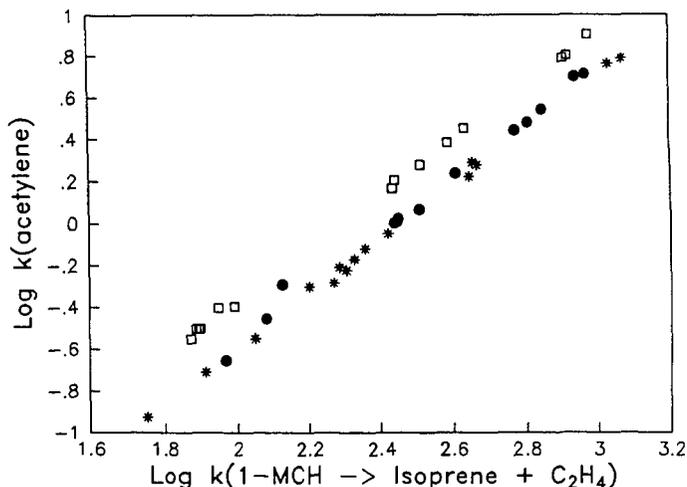


Table I: Typical Gas Analysis Results from the Decomposition of 1-Phenylbutene-2
(in units of 10³ x mole fraction)

A) Normalized against initial mixture (composition; 964, trans 1-PHb-2; 21, cis 1-PHB-2; 12, s-Butylbenzene; 2.6 n-Butylbenzene)

Mixtures	1% (1-PHB-2) in Argon	1% (1-PH-2) 200ppm (1-MCH) in Argon	1% (1,2,4TMB) .5% (1-PHB-2) 100ppm (1-MCH) in Argon	2% (1,2,4-TMB) .25% (1-PHB-2) 50 ppm (1-MCH) in Argon
Methane	8.3	6.6	5.8	11.4
Ethane, Ethene	6.9	2.0	4.2	8.2
Propylene	9.6	7.7	1.7	3.5
Acetylene	1.3	.81	.3	.74
Butenes	1.5	1.3	.45	.8
1,3 Butadiene	3.5	2.5	.76	1.7
Benzene	2.5	1.7	.57	1.2
Toluene	2.8	1.8	.82	1.8
Ethylbenzene	3.4	2.5	.5	1
m,p-Xylene			1.4	2.9
Styrene	6.5	5.0	2.0	3.6
o-Xylene			.5	1.0
Allylbenzene	5.8	4.6	1.1	2.1
s-Butylbenzene	7.4	8.5	11.2	8
n-Butylbenzene	2.2	2.2	2.3	2.5
1-PHB-2 trans	860	860	916	895
cis	62	57	30	76
			50	85
				961
				35

b) Normalized against 1-MCH

Isoprene	133	34	91	178	234	53
1-MCH	807	944	904	780	744	934
Temperature(K) (based on Isoprene yields)	1160	1105	1143	1172	1185	1121

Reaction Time: 500 microseconds; Pressure: 2.8-3.2 atm.