

DECOMPOSITION OF HIGHLY EXCITED BUTENYL AND PENTENYL RADICALS

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(Received June 10, 1985; in revised form September 2, 1985)

Summary

The unsaturated radicals 1-buten-1-yl, 1-buten-2-yl and 2-penten-3-yl were made highly excited by the chemical activation technique involving addition of a photochemically generated hot (about 23 kcal mol⁻¹) hydrogen atom to the acetylenic bond of the corresponding hydrocarbon. There are two different mechanisms of decomposition of the excited radical. (I) Breakage of the C—C bond is accompanied by the transformation of the adjacent single bond into a double bond. Another double bond, present in the radical, is too remote from the site of reaction to be of much importance. (II) Breakage of the C—C bond is accompanied by the transformation of the adjacent double bond into the acetylenic bond. The activated complex is looser than in case (I) and the *A* factor is correspondingly higher by 0.5 · 0.6 s⁻¹. Log *A*_I = 13.5 and log *A*_{II} = 14.0 at an optimized bond dissociation energy BDE(=CR···H) = 104.5 kcal mol⁻¹.

1. Introduction

In previous papers from this laboratory a variant of the chemical activation method has been described which is useful for obtaining highly excited alkyl radicals [1, 2]. The method is based on the addition of hot hydrogen atoms to the double bond of olefins. The hydrogen atoms are generated by the photolysis of either hydrogen sulphide or hydrogen iodide. The resulting radicals have about 13 - 34 kcal mol⁻¹ more excitation energy than those originating from the classical addition involving thermal hydrogen atoms. Thus, additional insight may be gained into the reactions of excited radicals.

The method, supported by Rice-Ramsperger-Kassel-Marcus (RRKM) calculations, has been applied to investigate unsaturated C₃H₅ radicals [3] and the kinetic information obtained was used to challenge the established mechanism of propylene photolysis. In the present work the study is extended to cover decomposition processes of unsaturated C₄H₇ and C₅H₉ radicals of different structure.

2. Experimental details

The main features of the experiments are the same as those described previously [1-3]. A medium pressure mercury resonance lamp was used as the source of light and the 185 nm line was filtered off. The range of pressures covered in these studies varied from 2 to 760 Torr. The conversion was kept as low as possible to avoid any secondary effects. The hydrocarbons were obtained from ICN Pharmaceuticals, Inc. 2-Butyne and 2-pentyne were additionally purified by distillation from a liquid nitrogen-toluene slush. 1-Butyne was purified by gas chromatography. Hydrogen sulphide, obtained from Merck, was purified by passing it over activated carbon. Dark reactions of hydrogen sulphide with the hydrocarbons of interest were not observed.

3. Results

Photolysis of mixtures of 1-butyne and hydrogen sulphide (60:40, by volume) leads to the formation of methane, acetylene, ethane, allene and 1-butene. The yield for acetylene is very close to that for ethane while the yield for methane is very close to that for allene. All these yields decrease with increasing pressure contrary to the yield for 1-butene which exhibits a marked increase. The yields for acetylene and allene are shown in Fig. 1 and Table 1. These yields are expressed in the form $W(C_2H_2) = P(C_2H_2)/\Sigma P$ and $W(\text{allene}) = P(\text{allene})/\Sigma P$. $P(C_2H_2)$ and $P(\text{allene})$ denote respective amounts of these hydrocarbons formed in the photolysis while

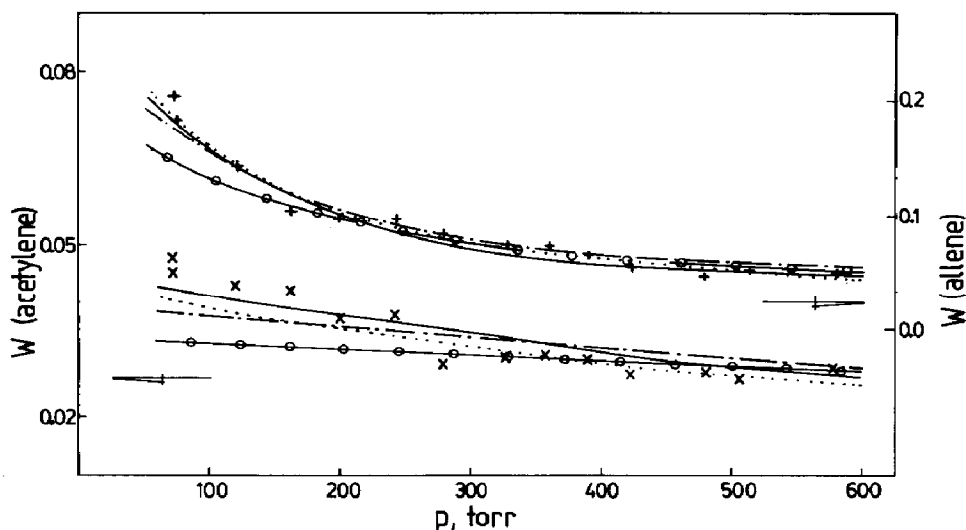


Fig. 1. Pressure dependence of the yields for allene and acetylene originating from the photolysis of 1-butyne-H₂S mixtures (BDE(=CR...H) = 104.5 kcal mol⁻¹): +, allene (experimental points); x, acetylene (experimental points); - - -, $\langle \Delta E \rangle$ for strong collision; —, $\langle \Delta E \rangle = 10 \text{ kcal mol}^{-1}$; - · -, $\langle \Delta E \rangle = 5 \text{ kcal mol}^{-1}$; -○-, $\langle \Delta E \rangle = 3 \text{ kcal mol}^{-1}$.

TABLE 1

Pressure dependence of the yields for acetylene and allene in the H₂S-1-butyne system and of the yield for propyne in the H₂S-2-butyne system

<i>1-Butyne</i>			<i>2-Butyne</i>	
<i>Pressure</i> (Torr)	<i>W(C₂H₂)</i>	<i>W(allene)</i>	<i>Pressure</i> (Torr)	<i>W(propyne)</i>
71	0.048	0.20	78.8	0.16
72	0.045	0.18	92.3	0.16
120	0.042	0.14	115.4	0.15
162	0.042	0.13	142.3	0.12
200	0.037	0.10	153.8	0.12
241.8	0.037	0.10	169.2	0.11
280	0.029	0.08	199.5	0.10
327.2	0.031	0.075	215.4	0.10
360	0.032	0.07	230.8	0.095
390.8	0.031	0.06	246.1	0.095
424	0.027	0.05	269.2	0.10
480	0.028	0.05	292.3	0.095
514.4	0.027	0.05	307.7	0.09
580	0.029	0.05	323.1	0.085
			346.1	0.08
			369.2	0.08
			384.6	0.075
			400	0.07
			423.1	0.075
			429.9	0.065
			453.8	0.05
			476.9	0.055
			500	0.05
			576.9	0.04
			692.3	0.035
			730.8	0.03

$\Sigma P = P(C_2H_2) + P(\text{allene}) + P(\text{1-butene})$. This method of presenting the results has been explained previously [1 - 3].

Photolysis of mixtures of 2-butyne and hydrogen sulphide (60:40, by volume) results in the formation of methane, propyne, 2-butenes and trace amounts of 1-butene. The pressure dependence of the propyne yield expressed as the ratio of propyne to the total propyne and *trans*- and *cis*-2-butenes is shown in Fig. 2 and Table 2.

Photolysis of mixtures of 2-pentyne with hydrogen sulphide yields methane, ethane, propyne, 1-butyne, 1,2-butadiene and 2-pentenenes. The yield for ethane is very similar to that for propyne while the yield for methane exceeds by about 5% - 20% the total yield for 1-butyne and 1,2-butadiene. The pressure dependence of the yields for 1-butyne and 1,2-butadiene is shown in Fig. 3 and Table 3. The yields were calculated as the ratios of the amount of the respective hydrocarbon to the total of propyne, 1-butyne, 1,2-butadiene and 2-pentenenes.

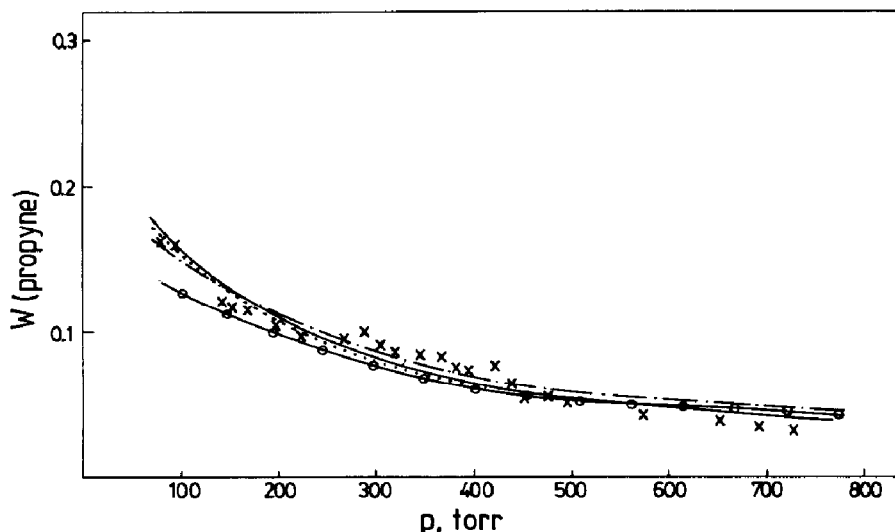


Fig. 2. Pressure dependence of the yield for propyne originating from the photolysis of 2-butyne-H₂S mixtures (BDE(=CR...H) = 104.5 kcal mol⁻¹): ×, experimental points; - - -, $\langle \Delta E \rangle$ for strong collision; —, $\langle \Delta E \rangle = 10$ kcal mol⁻¹; - · - ·, $\langle \Delta E \rangle = 5$ kcal mol⁻¹; —○—, $\langle \Delta E \rangle = 3$ kcal mol⁻¹.

TABLE 2

Pressure dependence of the yields for 1-butyne and 1,2-butadiene in the H₂S-2-pentyne system

Pressure (Torr)	W(1-butyne)	W(1,2-butadiene)
11.5	—	0.050
26.4	0.050	0.034
36.2	0.043	0.029
64	0.028	0.018
83.2	0.022	0.014
100.8	0.021	0.013
105.1	0.019	0.012
115.2	0.019	0.013
131.8	0.015	0.010
148.3	0.013	0.009
175.4	0.012	0.008
190.7	0.008	0.005
206.1	0.008	0.005
216	0.005	0.004

In all photolyses some amounts of mercaptans were formed apart from hydrocarbons as well as a polymer deposited onto the walls of the reaction vessel. To avoid the secondary photolysis of the mercaptans and polymers the reactor was cleaned thoroughly after every run. Cleaning with chromic acid was followed by rinsing with distilled water and drying at a temperature of 150 - 200 °C.

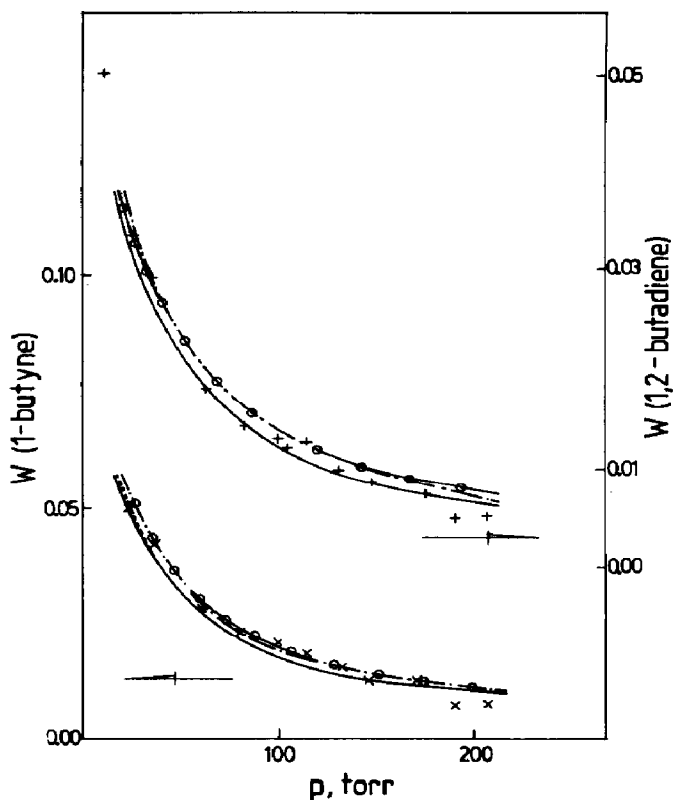


Fig. 3. Pressure dependence of the yields for 1,2-butadiene and 1-butyne originating from the photolysis of 2-pentyne–H₂S mixtures (BDE(=CR···H) = 104.5 kcal mol⁻¹): +, 1,2-butadiene (experimental points); x, 1-butyne (experimental points); - - -, $\langle \Delta E \rangle$ for strong collision; —, $\langle \Delta E \rangle = 10$ kcal mol⁻¹; - · -, $\langle \Delta E \rangle = 5$ kcal mol⁻¹; —○—, $\langle \Delta E \rangle = 3$ kcal mol⁻¹.

TABLE 3

Dissociation of the 1-buten-2-yl radical $\text{CH}_2=\dot{\text{C}}-\text{CH}_2-\text{CH}_3^* \longrightarrow \text{CH}_2=\text{C}=\text{CH}_2 + \text{CH}_3$

BDE(=CR···H) (kcal mol ⁻¹)	E^* (kcal mol ⁻¹)	E_0 (kcal mol ⁻¹)	$\langle \Delta E \rangle$ (kcal mol ⁻¹)	W	$\log A^a$	k_{RRKM} (s ⁻¹)
96.3	68.92	41.41	SC	0.38	14.24	1.3×10^9
			10	0.38		
			5	0.29		
			3	0.24		
100.0	65.22	37.71	SC	0.40	13.83	1.2×10^9
			10	0.36		
			5	0.32		
			3	0.22		
104.5	60.72	33.21	SC	0.33	13.50	1.7×10^9
			10	0.29		
			5	0.23		
			3	0.17		

SC, strong collision.

^aA is in reciprocal seconds.

4. Discussion

Photolysis of hydrogen sulphide with 254 nm photons results in the decomposition



It is firmly established that practically all SH radicals are formed as vibrationally cold. The kinetic energy of the hydrogen atoms is about 23 kcal mol⁻¹ [2, 3]. We have previously proved that some of the hydrogen atoms add to the olefin double bond in the first collision, transforming the kinetic energy of the hydrogen atom into the internal energy of the radical. The spectrum of the products is extremely simple. In the presence of hydrogen sulphide the occurrence of radical combinations and additions to the double bond is suppressed. Instead hydrogen transfer follows according to the reaction



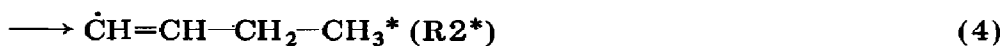
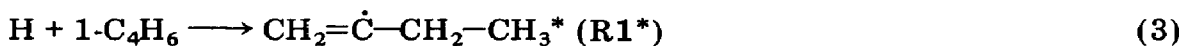
yielding stable products. Only unimolecular isomerizations and decompositions may occur prior to hydrogen sulphide scavenging.

This simplicity is the main advantage of the method since the analyses are easy and very accurate. The main drawback is the inability to determine the products of isomerizations that do not involve rearrangements of the carbon skeleton, since the products that differ only in the position of the radical site are indistinguishable in reaction (2). Another disadvantage is due to the specific reactions of HS radicals which induce effective cis-trans isomerizations and scavenge hydrocarbons that have coupled double bonds, such as 1,3-butadiene [4]. Therefore the isomerizations of the radicals studied in this work could not be examined fully and we confined ourselves to investigating decompositions of excited radicals.

It is worth mentioning that the removal of 1,3-butadiene from the determined reaction products results in an increase in the yields for all other products. The error cannot be estimated accurately since the yield of 1,3-butadiene is not known. Approximate calculations indicate that overestimations of the yields is less than 10% at lower pressures. The error decreases with increasing pressure.

4.1. Photolysis of hydrogen sulphide in the presence of 1-butyne

The formation of methane, acetylene, ethane and allene and the pressure dependences of the yields for these hydrocarbons can be explained by the occurrence of a sequence of reactions





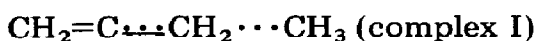
Methyl, ethyl and butenyl (R1 and R2) radicals abstract a hydrogen atom from hydrogen sulphide in reaction (2) yielding the corresponding hydrocarbons.

A conventional treatment of the experimental data involves an assumption of the steady state approximation to determine the dissociation rate constants and the yields $W(R1)$ and $W(R2)$ for the radicals formed in reaction (3) and reaction (4) respectively. However, the common assumption of strong collisions is not justified at large excitation energies [5 - 7] and the method may fail. Moreover, not every hydrogen atom adds to a double bond in the first collision. The presence of partly or completely thermalized hydrogen atoms is an additional difficulty since fewer excited radicals are formed, which affects the occurrence of decompositions at lower pressures [1, 2].

To calculate the pressure dependence of the yields for allene (reactions (5) and (6)) we used RRKM semiempirical calculations [8, 9]. The aim was to reproduce the experimental dependence by treating the structure of the activated complex, the yield $W(R1)$ for the 1-buten-1-yl radical and the amount of energy $\langle \Delta E \rangle$ exchanged in collisions as variables. A step-ladder model was assumed for the transfer of energy [8]. The assessment of the excitation energy E^* of the radicals and the threshold energy E_0 for reaction (5) is handicapped by the uncertainty associated with the magnitude of the dissociation energy for the vinyl bond. Since values scattered between 100 and 111 kcal mol⁻¹ (with many values in between) are reported in the literature [10, 11], the bond dissociation energy for =CR···H was out of necessity treated as one of the variables. The details of our RRKM calculations have been described previously [1 - 3]. Literature data [12, 13] and special procedures [14, 15] were used to fit the vibrational frequencies for the activated complex. The sums and densities of states were calculated by using Haarhoff's approximation [16]. Based on the data of Castelhana and Griller [17] the following bond dissociation energies at 0 K were used: CH₃···H, 102.8 kcal mol⁻¹; C_p···H, 98.5 kcal mol⁻¹; C_s···H, 94.5 kcal mol⁻¹. Enthalpies for hydrocarbon formation at 0 K were used as reported by Rossini *et al.* [18]. Activation energies for the reverse addition of the radicals to the unsaturated bonds were taken from the literature [13, 19]. Collisional frequencies were estimated by using the Lennard-Jones potential to calculate the corresponding cross sections.

The calculated results are inconclusive. It was possible to achieve a good agreement between calculated and experimental data over the pressure range 150 - 700 Torr, for different bond dissociation energies BDE(=CR···H) in the range 96.3 - 104.5 kcal mol⁻¹ and at different $\langle \Delta E \rangle$ starting with 3 kcal mol⁻¹. The results are shown in Table 3 and partly shown in Fig. 1. The effect of weak collisions is noticeable only at low pressures. Alterations in $\langle \Delta E \rangle$ affect the radical yields $W(R1)$. The values of

BDE(=CR...H) affect the structure of the activated complex to a large extent. Hence, the entropy of activation and the pre-exponential factors are also affected. This is due to the fact that E and E_0 depend in the same way on BDE(=CR...H) while the non-fixed energy of the activated complex, $E^\ddagger = E^* - E_0$, remains unchanged. With increasing excitation energy of the radicals the density of states also increases which, in turn, makes the use of a looser activated complex obligatory to obtain a similar value for the rate constant. Consequently the entropy of activation and the A factor are increased. Under such circumstances only $\log A$ for reaction (5) can be estimated. According to Benson, $\log A$ for the dissociation of the n -propyl radical is as low as 13.4 [13]. This value is so low because the activated complex is made rigid as the rotation of the single bond that is transformed into the double bond becomes hindered. This results in a decrease in both the entropy of activation and the A factor. The activated complex



involved in reaction (5) should have features similar to those of complexes involved in reactions of alkyl radicals. In this case the scission of the single C—C bond is accompanied by the transformation of the adjacent single bond into the double bond (complex I). The other double bond, removed by two bonds from the site of the reaction, is unlikely to be of much importance. It seems reasonable to assume that $\log A$ for this dissociation lies within the range 13.4 - 13.6 which corresponds to BDE(=CR...H) $\approx 104.5 \text{ kcal mol}^{-1}$. Further calculations to be commented on later support this tentative assessment. The frequency changes in going from the radical to the activated complex are listed in Table 4.

Similar calculations for reactions (4), (7) and (8) would yield very dubious results since the radical R2 is known to undergo efficient isomerization to the R3 structure [20]. The mechanism of this isomerization involves 1,4-hydrogen shifts:



Our experiments give no information on the occurrence of reaction (9). The reaction of R2 and R3 with hydrogen sulphide yields the same products while 1,3-butadiene, presumably formed in reaction (10), is scavenged completely by HS radicals. An attempt was made to estimate roughly the respective contributions of the dissociation and isomerization of the 1-buten-1-yl radical (reactions (7) - (11)) based on the following assumptions.

(a) BDE(=CH...H), an indispensable parameter for the thermochemical calculations, was assumed to be $108.5 \text{ kcal mol}^{-1}$, *i.e.* 4 kcal mol^{-1} higher than BDE(=CR...H). Following Carter and Tardy [15] the difference between the bond energies of the vinyls containing primary and secondary

TABLE 4

Frequency changes for the decomposition complex model

<i>Reaction</i>	<i>Radical</i>	<i>Complex</i>
CH=CHCH ₂ CH ₃ C ₂ H ₂ + C ₂ H ₅	950	0
	1346	673
	1168	584
	346(2)	173(2)
	990	600
	102	80
CH ₃ C=CHCH ₃ CH ₃ C≡CH + CH ₃	950	0
	1374	687
	1346	673
	950	475
	346	173
	900	500
	212	115
CH ₂ =CCH ₂ CH ₃ CH ₂ =C=CH ₂ + CH ₃ CH ₃ CH=CCH ₂ CH ₃ CH ₃ CH=C=CH ₂ + CH ₃	950	0
	1374	687
	1168	584
	950	475
	346	173
	212	125
	95	310
CH ₃ CH=CCH ₂ CH ₃ CH ₃ CH ₂ C=CH + CH ₃	950	0
	1374	687
	1346	673
	950	475
	403	201
	188	280
	650	400
	212	115

carbon atoms was assumed to be the same as the difference between the bond energies of primary and secondary alkyl radicals.

(b) Reaction (9) was investigated by Ibuki *et al.* [20] at an R2 excitation energy of 33 kcal mol⁻¹. We adopted the structure of the activated complex and the threshold energy determined by these Japanese researchers.

(c) The recommendations of Larson *et al.* [14] were used to construct the activated complex for R3 dissociation into 1,3-butadiene and a hydrogen atom.

The calculations were aimed at reproducing the experimental pressure dependence of the yield for acetylene. The details of the activated complex structure for reaction (7) (dissociation of 1-buten-1-yl into acetylene and ethyl radical), the yield $W(R2)$ for reaction (4) and $\langle \Delta E \rangle$ were varied to achieve the best fit. The final assessment between the calculations and the

experiment is not perfect as can be seen in Fig. 2. Nevertheless, bearing in mind the basic uncertainties involved in the calculations the agreement is satisfactory. The results are shown in Table 5. $\langle \Delta E \rangle$ practically does not alter the shape of the curves shown in Fig. 2; it does affect, however, the values for $W(\text{R2})$ which decrease from 0.08 for the strong collision assumption to 0.06 at $\langle \Delta E \rangle = 3 \text{ kcal mol}^{-1}$. The results indicate that the 1,4-hydrogen shift isomerization (reaction (9)) is competitive with the dissociation of R2. The reverse endothermic isomerization cannot compete effectively with the fast dissociation of R3 into 1,3-butadiene (reaction (10)). Since $\log A_{10}$ is large at relatively small E_0 , reaction (10) is likely also to be of importance in the system studied by Ibuki *et al.* [20]. These researchers suggested the disproportionation of radicals as the sole pathway for 1,3-butadiene formation in their experiments. Reaction (10) may be a prevailing channel. It should be noted that the value for A_7 is especially high, which indicates the existence of a loose complex. This will be commented on below.

TABLE 5

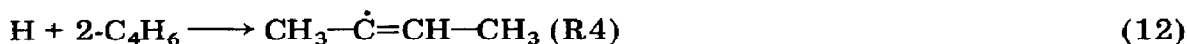
Reactions of 1-buten-1-yl and 1-buten-4-yl radicals

Reaction	Number	E^* (kcal mol^{-1})	E_0 (kcal mol^{-1})	$\log A^a$	k_{RRKM} (s^{-1})
1-Buten-1-yl $\longrightarrow \text{C}_2\text{H}_2 + \text{C}_2\text{H}_5$	7	56.7	30.5	14.06	8.2×10^9
1-Buten-1-yl \longrightarrow 1-buten-4-yl	9	56.7	17.1	12.22	6.6×10^9
1-Buten-4-yl \longrightarrow 1-buten-1-yl	-9	66.7	27.1	12.38	7.8×10^8
1-Buten-4-yl \longrightarrow 1,3-butadiene + H	10	66.7	31.0	13.87	2.8×10^{10}

^a A is in reciprocal seconds.

4.2. Photolysis of hydrogen sulphide in the presence of 2-butyne

The addition of hot hydrogen atoms to the acetylenic bond of 2-butyne followed by the dissociation of excited 2-buten-2-yl radicals explains the formation of propyne. Three other major products, methane and *cis*- and *trans*-2-butene, originate from the consecutive reaction of methyl and butenyl radicals with hydrogen sulphide



Calculations exactly similar to those concerning the R1 radical were performed. The results are shown in Table 6 and partly shown in Fig. 3. As previously found for all $BDE(=CR\cdots H)$ and for all $\langle \Delta E \rangle$ the calculated results can be matched with experiment. Our former choice, $BDE(=CR\cdots H) = 104.5 \text{ kcal mol}^{-1}$, corresponds to $\log A_{13} = 14.11$. This value is very similar to that for reaction (7). Such similarity is indeed expected. The activated complex



for both reactions (7) and (13), complex II, is essentially different from complex I. The rupture of the single C—C bond is accompanied by the transformation of the double bond into the acetylenic bond. In this case the complex should not be so rigid, and this should manifest itself by an increase in the entropy of activation by about 2 or 3 entropy units. Therefore, a plausible estimation for $\log A$ of reactions involving complex II falls within the range 13.9 - 14.2. Such values agree very well with those evaluated previously for C_3H_5 [3].

TABLE 6

Dissociation of the 2-buten-2-yl radical $CH_3-\dot{C}H=CH-CH_3^* \longrightarrow CH_3-C \equiv CH + CH_3$

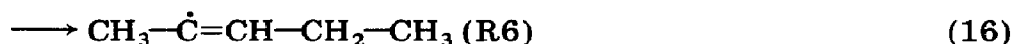
BDE(=CR \cdots H) (kcal mol $^{-1}$)	E^* (kcal mol $^{-1}$)	E_0 (kcal mol $^{-1}$)	$\langle \Delta E \rangle$ (kcal mol $^{-1}$)	W	$\log A^a$	k_{RRKM} (s $^{-1}$)
96.3	67.0	42.3	SC	0.28	14.94	2.3×10^9
			10	0.28		
			5	0.22		
			3	0.18		
100.0	63.3	38.6	SC	0.28	14.58	2.4×10^9
			10	0.27		
			5	0.20		
			3	0.20		
104.5	58.8	34.1	SC	0.27	14.11	2.4×10^9
			10	0.25		
			5	0.20		
			3	0.15		

SC, strong collision.

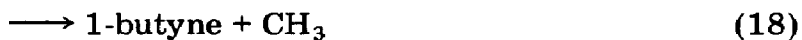
^a A is in reciprocal seconds.

4.3. Photolysis of hydrogen sulphide in the presence of 2-pentyne

Addition of a hydrogen atom to 2-pentyne yields two radicals:



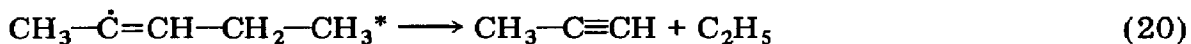
Such reactions involving thermal hydrogen atoms have been studied extensively [15]. R5 was found to undergo two-channel dissociation:



The ratio [1,2-butadiene]/[1-butyne] decreases with increasing pressure from 1.8 at $p = 0.016$ Torr to about 1.18 at higher pressures.

Our data confirm the occurrence of reactions (17) and (18). However, the ratio [1,2-butadiene]/[1-butyne] is much lower, 0.65 ± 0.02 , and does not depend on pressure within the range of pressures examined in this work. Apparently reaction (17) prevails at lower excitation energy and an enhancement in the contribution of reaction (18) is observed with increasing excitation energy.

Reactions of 2-penten-2-yl were also studied by Carter and Tardy [15]. Apart from the reaction



i.e. dissociation into ethyl radical and propyne, numerous isomerizations were found to occur: 1,4-hydrogen shifts, *cis-trans* isomerizations and skeletal rearrangements. As many as eight intermediary species were proposed by Carter and Tardy. Unfortunately, many dissociations lead to the formation of 1,3-butadiene. Since this product is not found in our experiments no new insight into the isomerizations can be gained. The yield for methane is higher than the total yield for 1,2-butadiene and 1-butyne. This is indirect evidence that 1,3-butadiene is formed in our system but vanishes having been scavenged by SH. Therefore we limited the RRKM calculations to reactions (17) - (19). The structure of the activated complex, the yield for 2-penten-3-yl, and $\langle \Delta E \rangle$, were varied as before to match the experimental data. $\text{BDE}(=\text{CR}\cdots\text{H}) = 104.5 \text{ kcal mol}^{-1}$ was used as previously recommended. The results are shown in Table 7 and in Fig. 4. The reproduction of the experimental results is satisfactory. Alterations in $\langle \Delta E \rangle$ only slightly affect the shape of the curves. However, the radical yield

TABLE 7

Dissociation of the 2-penten-3-yl radical

Reaction	Number	E^* (kcal mol^{-1})	E_0 (kcal mol^{-1})	$\log A^a$	k_{RRKM} (s^{-1})
1,2-Butadiene + CH_3	17	60.6	33.7	13.51	1.48×10^8
1-Butyne + CH_3	18	60.6	34.9	13.95	2.56×10^8

^a A is in reciprocal seconds.

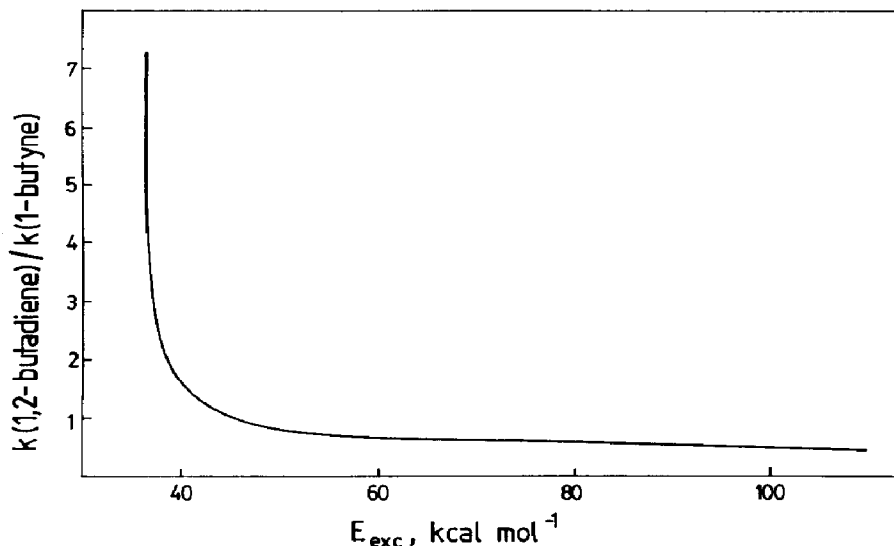


Fig. 4. Dependence of the ratios for two competitive rate constants of 2-penten-2-yl dissociation on the internal energy of the radical.

$W(\text{R5})$ decreases from the strong collision value of 0.2 to 0.125 at $\langle \Delta E \rangle = 3 \text{ kcal mol}^{-1}$. The dependence of the calculated ratio k_{17}/k_{18} on the radical internal energy is shown in Fig. 4. At low excitation energies ($E^* < 44 \text{ kcal mol}^{-1}$) k_{17} is larger than k_{18} , which is not surprising since the threshold energy for reaction (17) is lower. At higher excitation energies the differences in threshold energies are less important, the structure of the activated complex and hence $\log A$ become rate determining factors. These observations are useful in explaining the experimental ratios $[1,2\text{-C}_4\text{H}_6]/[1\text{-C}_4\text{H}_6]$ reported by Carter and Tardy [15]. These researchers evaluated the excitation energy of the R4 radical as $38.9 \text{ kcal mol}^{-1}$. In fact, the radicals formed as a result of thermal hydrogen addition to the acetylenic bond exhibit a considerable scatter in excitation energies. Thus, the rate constant is expected to increase with increasing pressure [21]. At lower pressures the energy distribution of the decomposing radicals closely resembles that of the formed radicals. At higher pressures, low energy radicals are stabilized effectively in collisions. The mean energy of the decomposing radicals increases and so does the ratio $[1\text{-C}_4\text{H}_6]/[1,2\text{-C}_4\text{H}_6]$. Such an interpretation involving the relative yields for two branching dissociation channels competing with each other depending on pressure has been frequently used and discussed for other systems [22 - 24].

The values assembled for $\log A$ in Table 7 agree well with the results obtained for the butenyl radicals and confirm our former conclusions. However, contrary to the present work, Carter and Tardy [15] did not observe any significant difference between $\log A_{17} = 13.69$ and $\log A_{20} = 13.78$. Such a difference is expected to exist since reaction (17) involves activated complex I while reaction (20) involves complex II. If the results of Carter and Tardy were correct the ratio $[1,2\text{-butadiene}]/[1\text{-butyne}]$

should be about unity at higher excitation energies. Our value of 0.65 ± 0.02 contradicts this supposition. The vibrational frequencies that are changed on going from the radical to the activated complex are listed in Table 4.

5. Conclusions

The data on the dissociation of unsaturated butenyl and pentenyl radicals in conjunction with the pertinent RRKM calculations indicate the occurrence of two distinct types of decompositions.

(I) The double bond is formed in the vicinity of the breaking single C—C bond. The activated complex is very similar to those encountered in the dissociation of alkyl radicals; as internal rotation becomes hindered the entropy of activation decreases.

(II) The breakage of the single C—C bond is accompanied by the formation of the acetylenic bond at the adjacent carbon atom. The activated complex is looser than in case (I).

The values of $\log A$ for both types of reactions depend strongly on the adopted bond dissociation energy of the vinyl group. Our results seem to favour $\text{BDE}(=\text{CR}\cdots\text{H}) = 104.5 \text{ kcal mol}^{-1}$. Then $\log A = 13.5$ and $\log A = 14.0$ for reactions of type I and type II respectively. The difference in $\log A$ is largely independent of BDE since both $\log A_{\text{I}}$ and $\log A_{\text{II}}$ are affected in much the same manner by the alterations in the bond dissociation energies.

To obtain more information on the reactions of highly excited unsaturated radicals additional investigations are needed. Hydrogen iodide could be used as another source of hydrogen atoms. Such experiments would yield complementary data on radical isomerizations.

Acknowledgment

A research grant from the Institute of Nuclear Research, Warsaw, is appreciated.

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