

## DISSOCIATION AND ISOMERIZATION OF EXCITED $C_3H_5$ RADICALS IN THE GAS PHASE

JAN NIEDZIELSKI, JANUSZ GAWŁOWSKI and TOMASZ GIERCZAK

Department of Chemistry, Warsaw University, Żwirki i Wigury 101, 02-089 Warsaw (Poland)

(Received July 1, 1982)

### Summary

Highly excited  $C_3H_5$  radicals were formed in the gas phase by the addition of hot hydrogen atoms ( $E = 22.9 \text{ kcal mol}^{-1}$ ) to either allene or propyne. The hydrogen atoms were generated by the action of UV radiation (253.7 nm) on  $H_2S$ .

2-propenyl radicals undergo mainly cleavage of the C—H bond yielding allene or propyne; the latter decomposition channel predominates. The main reaction of 1-propenyl radicals is cleavage of the C—C bond yielding methyl radicals and acetylene. Rice—Ramsperger—Kassel—Marcus calculations indicate that isomerization of the propenyl radicals into the allylic structure may be of importance. The calculations involving allyl radicals with an excess energy as high as about  $81 \text{ kcal mol}^{-1}$  demonstrate that dissociation yielding allene and a hydrogen atom is not effective; isomerization can occur prior to dissociation but the rate constants for both processes are markedly lower than that of the propenyl radical.

The implications of these results with respect to the determination of the photolysis mechanism for gaseous olefins are briefly discussed.

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### 1. Introduction

$C_3H_5$  radicals are believed to be important intermediates in the radiolysis and vacuum UV photolysis of gaseous olefins [1 - 10]. However, reliable kinetic data for the reactions of excited  $C_3H_5$  radicals are scarce, and even the mechanistic details of such reactions are unreliable. Most of the data are derived from analyses of the stable end products of the photolyses, and such a procedure can often lead to erroneous results. In this work the experimental technique of chemical activation using hot hydrogen atoms developed in our laboratory [11, 12] was used to study the reactions of  $C_3H_5$  radicals. The experiments were accompanied by theoretical calculations of the rate constants based on the Rice—Ramsperger—Kassel—Marcus (RRKM) theory of unimolecular reactions [13, 14].

## 2. Experimental details

Propyne was synthesized by the action of sodium ethanolate on 1,2-dibromopropane [15], and allene was synthesized by the action of zinc on 2,3-dibromopropylene [16]. The products contained less propylene, the most deleterious impurity, than commercial samples. A gas chromatography technique was used to remove the propylene together with other hydrocarbons which were present in smaller amounts. Propyne was removed from the allene by passing it through a short column filled with 25%  $\text{AgNO}_3$  in triethyleneglycol deposited onto Chromosorb P. However, despite rigorous purification small amounts of allene (20 - 30 ppm) remained in the propyne.  $\text{H}_2\text{S}$  was also synthesized and was distilled under vacuum to remove traces of hydrocarbons.

A quartz vessel of volume 0.4 l was used as the reactor. A Philips low pressure mercury resonance lamp was used as the light source. Since only the 253.7 nm line was required, the 184.9 nm line was cut off using an envelope made from thin polyethylene foil.

The photolytic products were analysed by gas chromatography. The hydrocarbon yields reported are averages of several determinations and are accurate to within 2% - 4%.

## 3. Results

Photolysis of propyne containing 10%  $\text{H}_2\text{S}$  resulted in the formation of propylene, allene, acetylene and methane. The yields of acetylene and methane were the same within the limits of experimental error. The ratios of the allene yield to the propylene yield and the acetylene yield to the combined acetylene and propylene yield are presented in Fig. 1.

Propylene, propyne and much smaller amounts of acetylene and methane were formed in the photolysis of allene containing 10%  $\text{H}_2\text{S}$  at 253.7 nm. As previously the yields of acetylene and methane were almost equal. The ratios

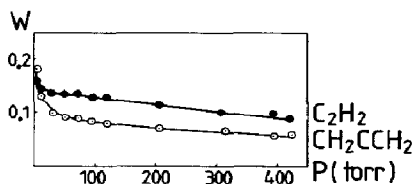


Fig. 1. Pressure dependence of the ratios of the allene yield to the propylene yield and the acetylene yield to the combined acetylene and propylene yield in propyne illuminated in the presence of 10%  $\text{H}_2\text{S}$ .

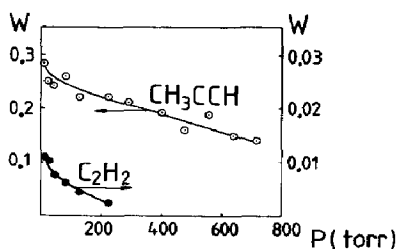


Fig. 2. Pressure dependence of the ratios of the propyne yield to the propylene yield and the acetylene yield to the propylene yield in allene illuminated in the presence of 10%  $\text{H}_2\text{S}$ .

of the propyne yield to the propylene yield and the acetylene yield to the propylene yield are shown in Fig. 2.

The formation of mercaptans (allyl and possibly other compounds) in addition to the hydrocarbons was established. Undesirable side reactions of the HS radicals with C<sub>3</sub>H<sub>4</sub> hydrocarbons could not be avoided even at the smallest H<sub>2</sub>S conversions. Therefore we were careful to maintain this conversion at such a level (always below 10%) that the hydrocarbon yields were not noticeably affected by the accumulation of mercaptans.

#### 4. Discussion

The exposure of C<sub>3</sub>H<sub>4</sub>-H<sub>2</sub>S mixtures to UV light with a wavelength of 253.7 nm resulted in the formation of hot hydrogen atoms from the photolysis of H<sub>2</sub>S (preliminary experiments in the absence of H<sub>2</sub>S did not reveal any chemical changes):



The energy of hydrogen atoms calculated using the thermochemical data given in Table 1 and taking into account the law of conservation of momentum is  $E = 22.91 \text{ kcal mol}^{-1}$  (the activation energies for the addition of hydrogen atoms to allene and propyne and for the addition of methyl radicals to acetylene were taken from the literature [18, 24 - 26]). Previous results obtained using classical hot atom chemistry techniques [27] and the latest laser-induced fluorescence measurements of the internal energy distribution of HS indicate beyond any doubt that it is both vibrationally and rotationally cold [28 - 30].

TABLE 1

Thermochemical data <sup>a</sup>

	$\Delta H_f^\circ$	Reference		Reference
Propyne	46.017	[17]	$S^\circ(300 \text{ K})(\text{CH}_3\dot{\text{C}}\text{HCH}) = 67.3$	[18]
Allene	47.7	[17]	$S^\circ(300 \text{ K})(\text{CH}_3\dot{\text{C}}\text{CH}_2) = 67.3$	[18]
$\dot{\text{C}}\text{H}_2-\dot{\text{C}}\text{H}-\dot{\text{C}}\text{H}_2$	41.54 <sup>b</sup>		$S^\circ(300 \text{ K})(\text{allyl}) = 62.1$	[21]
H	51.63	[22]	$D(:\text{CH}-\text{H}) = 100.3$ <sup>c</sup>	
CH <sub>3</sub>	35.8	[22]	$D(:\text{CR}-\text{H}) = 96.8$ <sup>d</sup>	
C <sub>2</sub> H <sub>2</sub>	54.48	[22]		
C <sub>3</sub> H <sub>6</sub>	8.47	[17]		

<sup>a</sup>All values are given in kilocalories per mole and refer to a temperature of 0 K unless stated otherwise.

<sup>b</sup>Based on an allyl resonance energy of 11.5 kcal mol<sup>-1</sup> [19, 20].

<sup>c</sup>Based on the enthalpies of formation of the vinyl radical and ethylene at a temperature of 0 K [22].

<sup>d</sup>A value 3.5 kcal mol<sup>-1</sup> lower than  $D(:\text{CH}-\text{H})$  is assumed, as was done in the case of the energy for the dissociation of hydrogen atoms from primary and secondary carbon atoms in alkanes [23].

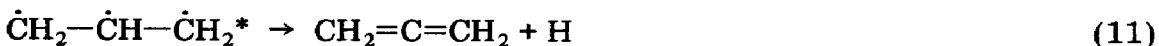
Wagner and Zellner in their studies of the reaction of thermal hydrogen atoms with allene [24] and propyne [25] established a mechanism that explains our results satisfactorily if H<sub>2</sub>S is assumed to have the double role of a source of hot hydrogen atoms and a free-radical scavenger. Of all the possible reactions of hot hydrogen atoms only addition to the double bond is likely to occur. Other reactions such as hydrogen atom abstraction and substitution need not concern us here. Arguments analogous to those advanced for mixtures of 1-butene and H<sub>2</sub>S [12] can readily be invoked:



2-propenyl



1-propenyl



allyl



The kinetic examination of such a sequence of reactions is not easy. This is due both to the limitations of the method used and to the behaviour of the system under investigation.

(1) Not all the hot hydrogen atoms add to the double bond in the first collision; the majority of them undergo thermalization and subsequent addition, yielding radicals that have a lower excitation energy.

(2) Collisionally stabilized 1- and 2-propenyl radicals react with H<sub>2</sub>S to yield the same product, *i.e.* propylene (reactions (14) and (15)).

(3) Dissociation of the 2-propenyl radical (reactions (6) and (7)) is the reverse of the process by which it forms (reactions (2) and (4)). Thus a new generation of hydrogen atoms is formed. These atoms have a lower energy than those produced by the dissociation of H<sub>2</sub>S but can take part in reactions (2) and (4) or abstract hydrogen from H<sub>2</sub>S:



(4) The fate of the collisionally stabilized allyl radical is not known. However, it has been established that it is reluctant to abstract a hydrogen atom from  $\text{H}_2\text{S}$ .

(5) All the kinetic rate constants reported in this work were calculated on the basis of the strong collision hypothesis and this may fail at the energies present under our experimental conditions. We have discussed this problem elsewhere [12] and we believe that the errors due to the failure of the strong collision model are less than those arising from the problems discussed in points (1) - (4).

#### 4.1. Allene-hydrogen sulphide

If we neglect reaction (16), which competes with reactions (2) and (3), and reactions involving the allyl radicals, we can assume that all the hydrogen atoms adding to allene yield propylene at pressures above 100 Torr. Therefore  $w(\text{C}_3\text{H}_6) = 1$  where  $w$  denotes the yield for each hydrogen atom undergoing addition. The error introduced by these assumptions should not be too large because there is a large hydrocarbon excess. The occurrence of isomerization reactions should also be included in the mechanism:



When the stationary state approximation is applied to reactions (6) - (8) and (17) and (18) an expression of the familiar Stern-Volmer type is obtained:

$$\frac{1}{w(\text{propyne})} = \frac{1}{w(\text{R}^*)} \left( \frac{k_6 + k_7 + k_{17} + k_{18}}{k_6} + \frac{\omega}{k_6} \right) \quad (I)$$

where  $w(\text{R}^*)$  is the yield of excited 2-propenyl radical formed in the first collision of hot hydrogen atoms with allene and  $\omega$  is the collisional frequency ( $\omega = 1.88 \times 10^7 p$  where  $p$  is in torrs). The Lennard-Jones potential model was used to estimate the necessary cross sections [31]; the same values of  $\sigma$  and  $\epsilon/k$  were used for allene and propyne and values intermediate between those for propyne and for propylene were used for the  $\text{C}_3\text{H}_5$  radicals.

The pressure dependence of the reciprocal propyne yield is shown in Fig. 3. The line is satisfactorily straight at pressures above about 100 Torr. The ratio of the intercept to the slope gives an overall rate constant  $\Sigma k$  of  $2.1 \times 10^{10} \text{ s}^{-1}$  for the reactions of the 2-propenyl radical. This value is a rough estimate in view of the approximations discussed above, and the scatter of the experimental results also contributes to the uncertainty. Unfortunately the value of  $w(\text{R})$  is unknown and hence the determination of a separate value for  $k_6$  is not possible. The presence of acetylene and methane among the photolytic products (although in much smaller amounts than propyne or propylene) indicates isomerization of the 2-propenyl or allyl radicals to the 1-propenyl structure followed by its decomposition. This problem will be discussed further later.

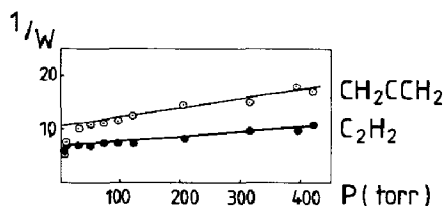
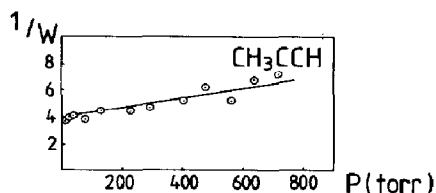


Fig. 3. The pressure dependence of the reciprocal propyne yield in the photolysis of allene containing 10%  $\text{H}_2\text{S}$ .

Fig. 4. The pressure dependence of the reciprocal yields of allene and acetylene in the photolysis of propyne containing 10%  $\text{H}_2\text{S}$ .

#### 4.2. Propyne-hydrogen sulphide

The 1-propenyl radical dissociated in reaction (9) does not yield hydrogen atoms. Hence it follows that the combined yield of propylene and acetylene is unity. Following this line of reasoning we can obtain from the data shown in Fig. 4 the following value for the overall unimolecular rate constant of the 2-propenyl radical:  $k_6 + k_7 + k_{17} + k_{18} = 1.3 \times 10^{10} \text{ s}^{-1}$  (the calculations are based on the yield of allene). An analogous value is obtained for the 1-propenyl radical:  $k_9 + k_{19} + k_{20} + k_{21} = 1.5 \times 10^{10} \text{ s}^{-1}$  (the calculations are based on the yield of acetylene) for



The estimated rate constants are high. This is not surprising because the radicals are very energetic (the effect of the exothermicity of the addition of a hydrogen atom to the double bond is augmented by the fact that the hydrogen atoms are hot). The excitation energies calculated using the appropriate thermochemical values (see Table 1 and refs. 18 and 24 - 26) are summarized in Table 2. These results are average values. The slight broadening is due to the Boltzmann distribution of the rotational energy of  $\text{H}_2\text{S}$  and the

TABLE 2

Excitation energies of  $\text{C}_3\text{H}_5$  radicals

Reaction	Excitation energy ( $\text{kcal mol}^{-1}$ ) for the following radicals		
	2-propenyl	1-propenyl	Allyl
H + allene	68.66	—	80.76
H + propyne	67.07	63.57	—

mean oscillation energy of either allene ( $E = 0.62 \text{ kcal mol}^{-1}$ ) or propyne ( $E = 0.72 \text{ kcal mol}^{-1}$ ) and to the mutual orientation of the momenta of the hydrogen atom and the hydrocarbon on collision. This broadening has a negligible effect on the values of the unimolecular rate constants for the radical reactions [32].

In general little information is obtained from the experiments.

(1) The decomposition of excited 2-propenyl radicals yields both allene and propyne. The contributions of these two dissociation channels cannot be determined directly. However, an approximate assessment is possible. The yield of the excited 2-propenyl in reaction (2) can be assumed to be twice as high as that in reaction (4) (there are two sites in the allene molecule that can be attacked by the hydrogen atom as opposed to only one such site in the propyne molecule). Hence  $w_2(\text{R}^*)/w_4(\text{R}^*) = 2$ . The intercepts from Figs. 3 and 4 give

$$\frac{1}{w_2(\text{R}^*)} \frac{k_6 + k_7 + k_{17} + k_{18}}{k_6} = 4$$

$$\frac{1}{w_4(\text{R}^*)} \frac{k_6 + k_7 + k_{17} + k_{18}}{k_7} = 10.6$$

Hence  $k_7/k_6 \approx 0.75$ . The rate constants for both reactions are similar but the channel yielding propyne appears to predominate.

(2) The yield of reaction (9) can be roughly assessed with respect to other reactions of the 1-propenyl radical by assuming that the contribution of the non-terminal addition of hot hydrogen atoms to propyne is the same as that to propylene, *i.e.*  $w_5(\text{CH}_3\text{CHCH}) = 0.19$  [33]. From this value we obtain

$$\frac{k_9}{k_9 + k_{19} + k_{20} + k_{21}} = 0.75$$

Reaction (9) appears to be the main pathway for the unimolecular reactions of the 1-propenyl radicals.

(3) The isomerizations of the 2-propenyl and allyl radicals into the 1-propenyl structure are of little importance as is shown by the low yield of acetylene in the allene-hydrogen sulphide system.

#### 4.3. Rice-Ramsperger-Kassel-Marcus calculations of the rate constants for the reactions of $\text{C}_3\text{H}_5$ radicals

The uncertainty concerning the fate of the allyl radicals and the difficulties experienced in the experimental determination of the contributions of the different reaction channels prompted us to perform RRKM calculations of the individual rate constants. Such calculations have already been performed but only some of the reactions and radicals were taken into account [1 - 6, 34]. The results will necessarily be approximate because the theory does not state explicitly how to construct the activated complexes. We have followed the procedures of Benson [21] with respect to the Arrhenius

coefficients and those of Larson *et al.* [35] with respect to the structure of cyclic complexes. The sums and densities of states were calculated using the Bayer-Swinehart algorithm [36] as modified by Stein and Rabinovitch [37, 38] (the BSSR algorithm) in steps of  $10 \text{ cm}^{-1}$ . The hindered rotations were treated as Pitzer's rotors; pertinent corrections to the excitation energy were introduced where necessary according to the procedure described by Stein and Rabinovitch. The corrections were not usually significant, *e.g.* in the case of 1-propenyl where the barrier height was assumed to be similar to that of propylene ( $H = 700 \text{ cm}^{-1}$  [21]) the density of states was only about 10% lower than that obtained using a free-rotation calculation. The crucial difficulty was the assessment of the values of the threshold energies of isomerization reactions involving cyclic complexes. In the absence of other data we used the relationship  $E_0 = E_s + E_{ab}$  [39] where  $E_s$  is the strain energy of the ring and  $E_{ab}$  is the activation energy of hydrogen atom abstraction by the radical ( $E_{ab} = 8 \text{ kcal mol}^{-1}$  was used throughout). The most reliable data are given in Tables 3 - 5.

The main dissociation channel of the decomposition of 2-propenyl is reaction (6) which yields propyne. The large value of the Arrhenius coefficient is due to the persistence of the rotations of the methyl group in the activated complex.  $k_7/k_6$  is about 0.4, *i.e.* lower than that previously estimated from the experimental data ( $k_7/k_6 = 0.75$ ). The reduction by a factor of 2 does not unduly impair the reliability of these data. In the case of the 1-propenyl radical the main process is cleavage of the C—C bond to give the methyl radical and acetylene. The calculated yield of this channel is 0.7, in excellent agreement with that previously assessed (also 0.7). Our value for  $\log A_9$  is higher than the value reported for the similar decomposition of *n*-propyl radicals yielding the methyl radical and ethylene ( $\log A = 13.4$  [21]). This can be explained by the differences in the structures of the activated complexes. The dissociation of *n*-propyl involves the disappearance of rotations of the  $\text{CH}_3\text{CH}_2\text{—CH}_2$  bond, contrary to the situation involved in the cleavage of the unsaturated  $\text{CH}_3\text{CHCH}$  radical.

TABLE 3

The numerical values of the calculated unimolecular rate constants for the reactions of the 2-propenyl radical

Reaction	Number	log A	$E_0$ (kcal $\text{mol}^{-1}$ )	Values for $E^* = 67.1$ kcal $\text{mol}^{-1}$		Values for $E^* = 68.7$ kcal $\text{mol}^{-1}$	
				$E^\ddagger$ (kcal $\text{mol}^{-1}$ )	$k$ ( $\text{s}^{-1}$ )	$E^\ddagger$ (kcal $\text{mol}^{-1}$ )	$k$ ( $\text{s}^{-1}$ )
Allene + H	7	13.42	47.7	19.4	$3.2 \times 10^9$	21.0	$4.6 \times 10^9$
Propyne + H	6	13.74	46.0	21.1	$8.3 \times 10^9$	22.7	$11.5 \times 10^9$
Allyl	17	12.86	35.0	32.1	$7.25 \times 10^9$	33.7	$9.4 \times 10^9$
1-propenyl	18	13.4	> 60	< 7.1	$< 4.1 \times 10^6$	< 8.7	$< 7.6 \times 10^6$



TABLE 4

The numerical values of the calculated unimolecular rate constants for the reactions of the 1-propenyl radical

Reaction	Number	log A	$E_0$ (kcal mol <sup>-1</sup> )	$E^\ddagger$ (kcal mol <sup>-1</sup> )	$k$ (s <sup>-1</sup> )
CH <sub>3</sub> + C <sub>2</sub> H <sub>2</sub>	9	13.95	40.84	22.73	1.4 × 10 <sup>10</sup>
Propyne + H	19	13.7	44.0	19.53	3 × 10 <sup>9</sup>
Allyl	21	12.9	35.1	28.47	2.9 × 10 <sup>9</sup>
2-propenyl	20	13.2	≈ 60	≈ 4	≈ 1 × 10 <sup>5</sup>

TABLE 5

The numerical values of the calculated unimolecular rate constants for the reactions of the allyl radical

Reaction	Number	log A	$E_0$ (kcal mol <sup>-1</sup> )	$E^\ddagger$ (kcal mol <sup>-1</sup> )	$k$ (s <sup>-1</sup> )
Allene + H	11	13.74	60.5	20.26	2.4 × 10 <sup>8</sup>
1-propenyl	23	13.5	50.7	30.06	1.5 × 10 <sup>9</sup>
2-propenyl	22	13.3	47.1	33.66	2.6 × 10 <sup>9</sup>

The very high values obtained for the rate constants of the isomerization of propenyl into allyl radicals are conspicuous. Ibuki *et al.* [34] investigated reaction (21) using the 1-propenyl radicals obtained by the addition of the methyl radical to acetylene. Their estimate of the threshold energy of this reaction is 34.5 kcal mol<sup>-1</sup>. Since our thermochemical data and our activated complex (constructed according to the procedure developed by Rabinovitch) are rather different from those used by the Japanese workers, we used the experimental data of Ibuki *et al.* to choose the best value for the  $E_0$ . A value of 35.1 kcal mol<sup>-1</sup> gave the best fit and therefore this value is included in Table 4. The contribution of isomerization increases at the expense of dissociation (reactions (9) and (19)) with decreasing excitation energy.

The high value for the isomerization of 2-propenyl into allyl is dubious. The contribution of this channel is about 38% over the range of energies covered by our calculations. According to Collin and Więckowski [3] this reaction cannot compete with dissociation. Perhaps our value for the threshold energy ( $E_0 = 35$  kcal mol<sup>-1</sup>) is too low.

The mutual isomerization of 1- and 2-propenyl radicals is very slow. The energy barrier is high owing to the strain energy of the cyclopropylene ring ( $E_s = 53.7$  kcal mol<sup>-1</sup> [21]).

The calculations concerning the allyl radicals appear to be the most unreliable (see Table 5). The values for the threshold energies are uncertain.

We used the  $E_0$  values for the corresponding reverse reactions augmented by the enthalpies because all these reactions are endothermic. The attribution of the oscillation skeletal and torsional frequencies in the allyl radical is also questionable. We were guided by the difference in the Arrhenius parameters for isomerization into both sides ( $\log A_1 - \log A_{-1} = 0.9$  based on the entropies in Table 1). The values reported in Tables 3 - 5 give 0.34 for the isomerization of 1-propenyl into allyl and a value of 0.5 for the analogous rearrangement of 2-propenyl into allyl. This is acceptable in view of the uncertainty concerning the entropies of the  $\text{CH}_3\dot{\text{C}}\text{CH}_2$  and  $\text{CH}_3\text{CH}\dot{\text{C}}\text{H}$  radicals. Because of these uncertainties further refinement of the calculations to achieve better agreement, although feasible, would be unproductive. The calculations show convincingly that isomerization rather than dissociation yielding allene is the predominant reaction channel. The rate constants of the allyl are much lower than those calculated for the corresponding reactions of the propenyl radicals regardless of its high excitation energy caused by the high  $E_0$  values due to the thermochemical stability of the allylic structures.

Thus the formation of acetylene under our experimental conditions as a result of the addition of hot hydrogen atoms to allene is due to the isomerization of the excited allyl radical into the 1-propenyl structure which subsequently decomposes.

Since  $E_0$  ascribed to reaction (17) is likely to be too low,  $E_0$  for the reverse reaction



will necessarily be higher than the value of 47.1 kcal mol<sup>-1</sup> inserted in Table 5. Thus in practice the dominant channel in reactions of the allyl radical may be the rearrangement into the 1-propenyl structure.

Since the rate constants for reactions of the allyl radical are in general low this radical is expected to be stabilized readily by collisions particularly at high pressures.

## 5. Conclusion

The reactions of excited  $\text{C}_3\text{H}_5$  radicals are multidirectional as is shown by RRKM calculations. The agreement between the experimental and theoretical estimates is satisfactory. However, if correct, these results imply that a critical reappraisal of the accepted olefin photolysis mechanism is required. Either our calculations, particularly those concerning the allyl radical, are erroneous or the ostensibly firmly established mechanism of olefin photolysis is wrong. It is not our purpose to discuss this in detail here but some examples taken from our work [7 - 9] and from that of Collin and coworkers [1 - 6] are given.

(1) It has been assumed that both allene and propyne originate from the reactions of excited allyl radicals in the photolysis of 1-butene and 1-pentene.

(2) The formation of allene and propyne in the photolysis of *cis*- and *trans*-2-butene has been explained by the dissociation and isomerization of the 1-propenyl radical.

(3) The 2-propenyl radical has been assumed to be the sole precursor of both allene and propyne in the photolysis of isobutene ( $\phi(\text{allene})/\phi(\text{propyne}) = 1.5$ ). The inadequacy of this mechanism has already been noted by Collin [5].

Thus, the problem of the formation of such important products as allene and propyne in the photolysis of olefins remains unsolved. The clue to the solution is likely to be found in the theoretical work of Evleth and Sevin [40]. These workers argue that an electronically excited ethylene molecule undergoes efficient 1,2 hydrogen shifts. If these processes were to occur in higher olefins (accompanied by rupture of the C—H bonds) some of the experimental data could readily be explained. Further evidence that such processes do occur can be inferred from the occurrence of various types of isomerization involving hydrogen shifts in the low energy (185 - 229 nm) photolysis of 2-methyl-2-butene [6]. Efficient fragmentation followed by secondary decomposition would impede the observation of such processes at higher energies. Further investigations, both theoretical and experimental, are required to elucidate all the details of these processes.

### Acknowledgment

The award of Research Grant 3.12.02.02 from the Institute of Nuclear Research, Warsaw, is appreciated.

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