

REACTION OF PHOTOCHEMICALLY GENERATED HOT HYDROGEN ATOMS WITH 1-BUTENE

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Summary

The reaction of hot hydrogen atoms with 1-butene was studied in the gas phase at pressures in the range 0.4 - 400 Torr (0.5 - 533 hPa). Hydrogen atoms were generated by exposing HI to the action of UV light ($\lambda = 334$ and 313 nm).

Some of the hydrogen atoms add to the double bond in a first collision yielding highly excited *sec*-butyl and *n*-butyl radicals; the remainder undergo thermalization according to a step-ladder model. The evidence that hot hydrogen atom addition occurs is based on kinetic considerations — both experimental and calculated RRKM rate constants for decomposition of the excited butyl radicals are given — and is supported by the observation that the contribution of non-terminal addition of hot hydrogen atoms reaches a level of about 30%, whereas thermal hydrogen atoms add mainly (about 94%) to the terminal carbon atom.

The hot hydrogen atom + olefin chemical activation technique provides an interesting tool for the investigation of highly excited radicals.

1. Introduction

There are many reports that hydrogen atoms formed in the radiolysis and the vacuum UV photolysis of olefins have excess kinetic energy [1, 2]. The reactions of such hot hydrogen atoms have not been studied extensively. Woolley and Cvetanović [3] as well as some other authors [4, 5] have reported that hot hydrogen atoms may undergo a double bond addition reaction with an olefin; the additional energy contributed (over that due to the exothermicity of thermal hydrogen atom addition) causes an increase in the rate constant for the decomposition of energized radicals.

It is attempted in this work to investigate the reaction of hot hydrogen atoms with 1-butene, and to establish to what extent the excess energy of the hydrogen atoms affects the butyl radical decomposition. To this end

mixtures of 1-butene and hydrogen iodide were exposed to the action of UV light of wavelengths 313 and 334 nm. HI served both as a source of hot hydrogen atoms and as an interceptor of radicals. 1-Butene was chosen as a model hydrocarbon to begin with for two reasons.

(1) It has previously been suggested that radiolysis and vacuum UV photolysis of 1-butene yield hot hydrogen atoms.

(2) The expected product of hydrogen atom addition — the excited *sec*-butyl radical — has been perhaps the most thoroughly discussed among the many studied by Rabinovitch in his classical works on chemical activation by the addition of thermal hydrogen atoms to olefins [6 - 8].

2. Experimental

2.1. Materials

1-Butene (Phillips research grade) was further purified gas chromatographically using an Al_2O_3 column until it contained no detectable traces of *n*-butane and lighter hydrocarbons. Hydrogen iodide was synthesized and subsequently distilled under vacuum; it contained no hydrocarbons. Since HI was found to react with vacuum greases yielding hydrocarbons (*e.g.* propylene), greaseless stopcocks were used.

2.2. Irradiation procedures

The experiments were carried out with a conventional Pyrex vacuum system. A 0.4 l quartz spherical vessel served as the reactor. A Tungoram 125 W medium pressure mercury lamp was used with appropriate chemical filters to cut off the unnecessary higher energy radiation. Naphthalene (1%) in *n*-propyl alcohol and an aqueous solution (0.5%) of potassium hydrogen phthalate (layers 1 cm thick) were used at 334 and 313 nm respectively. In the 313 nm experiments about 7% of the absorbed radiation originated from the 334 nm line. The exposure times ranged from 5 min to 10 h to keep the conversion of HI below 1% at lower pressures; at higher pressures this conversion was even smaller. The photolytic products were determined by gas chromatography. The analyses of hydrocarbons were estimated to be accurate to within 2 - 3%.

3. Results

The exposure of 1-butene containing 10% HI to the action of UV light resulted in the formation of methane, ethane, ethylene, propylene and *n*-butane. Neither organic iodides nor other hydrocarbons could be detected, except for very small quantities of 3-methylheptane and even smaller quantities of *n*-octane. The contribution of *n*-butane increased with increasing pressure at the expense of the contribution of four lighter hydrocarbons (methane, ethane, ethylene and propylene). The ratio of the yield of ethyl-

ene to that of ethane (calculated in arbitrary units and referred to as w) was almost unity ($w(\text{C}_2\text{H}_4)/w(\text{C}_2\text{H}_6) = 1 \pm 0.03$). The same proved to be true for the ratio $w(\text{C}_3\text{H}_6)/w(\text{CH}_4) = 1 \pm 0.05$. Both values were found to be independent of pressure. The greater scatter in the latter case was probably due to the less accurate methane determination. The yield for 3-methylheptane was no greater than 2% of that for *n*-butane; the results were not reproducible — in some experiments 3-methylheptane was almost not detectable.

The dependences of the relative yields for propylene, C_2 hydrocarbons (half of the total for ethylene and ethane) and *n*-butane on pressure are shown in Figs. 1 and 2. It is assumed that the total of the product yields (in arbitrary units) is unity:

$$w(\text{C}_3\text{H}_6) + w(\text{C}_2) + w(n\text{-C}_4\text{H}_{10}) = 1$$

where

$$w(\text{C}_2) = \frac{1}{2} \{w(\text{C}_2\text{H}_4) + w(\text{C}_2\text{H}_6)\}$$

The contribution of the 334 nm line of about 7% is allowed for in calculations concerning $\lambda = 313$ nm. The changes due to this correction are slight.

4. Discussion

The reaction of thermalized hydrogen atoms with 1-butene has been studied extensively [6 - 9]. The terminal addition of hydrogen atoms prevails yielding *sec*-butyl radicals:



Non-terminal addition also occurs but only to the extent of 5 - 6%:



The butyl radicals formed decompose essentially by C—C bond rupture; hydrogen atom rupture has been calculated to proceed at a thousandth of the C—C split rate. Collisional stabilization competes with dissociation. The principal secondary reactions following reactions (1) and (2) are



In these studies the hydrogen atoms were generated either in electrical discharges or photolytically using mercury photosensitization to bring about the decomposition of a hydrogen molecule. The experimental conditions were such as to warrant complete thermalization of the hydrogen atoms.

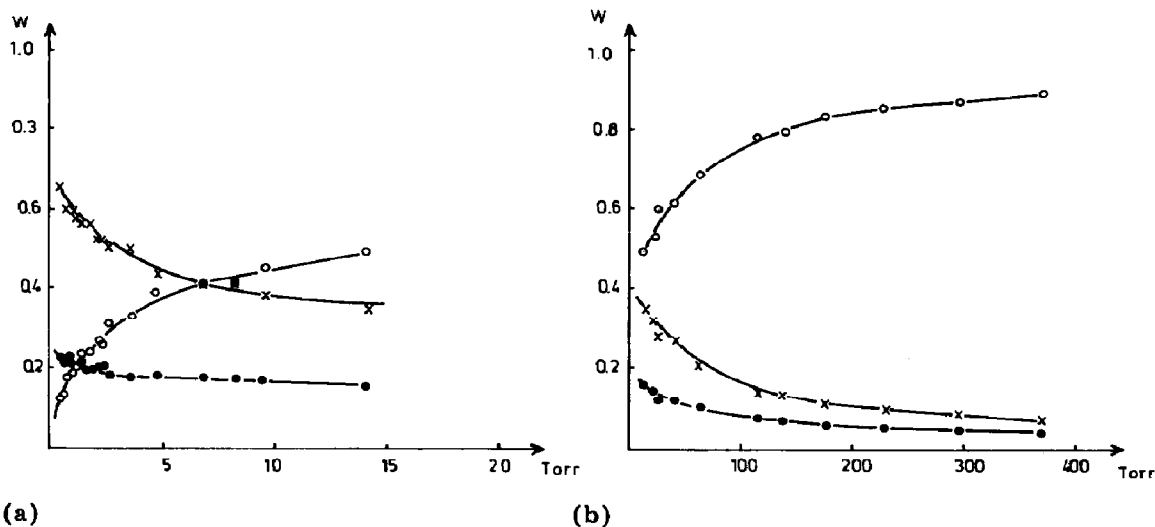


Fig. 1. The photolysis of 10% HI + 1-C₄H₈ showing the pressure dependence of the product yields: ●, $w_{C_2} = \frac{1}{2}(w_{C_2H_4} + w_{C_2H_6})$; X, $w_{C_3H_6}$; ○, $w_{n-C_4H_{10}}$. (a) Low pressure region; (b) high pressure region; $\lambda = 313$ nm.

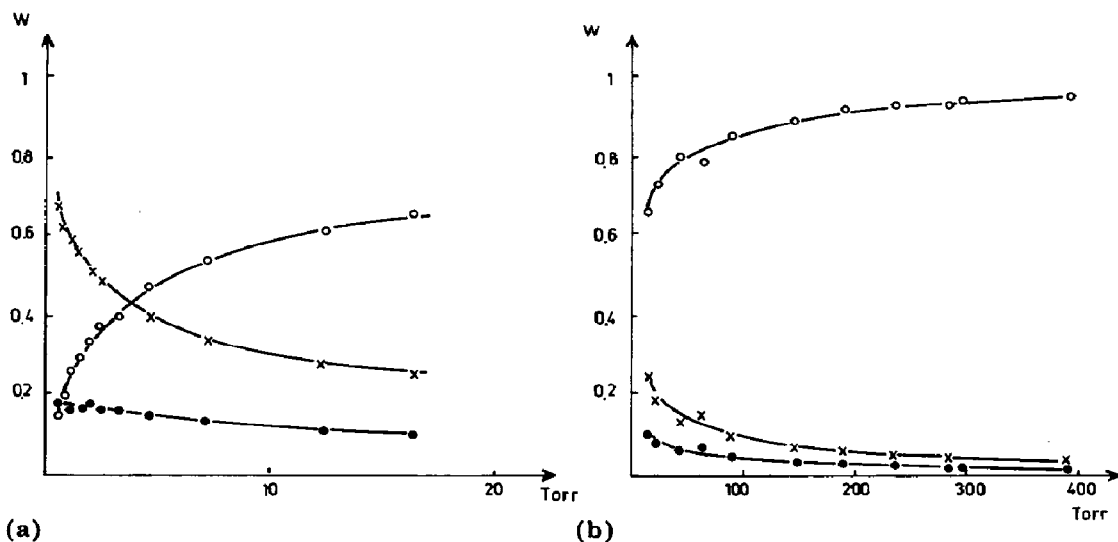


Fig. 2. The photolysis of 10% HI + 1-C₄H₈ showing the pressure dependence of the product yields: ●, $w_{C_2} = \frac{1}{2}(w_{C_2H_4} + w_{C_2H_6})$; X, $w_{C_3H_6}$; ○, $w_{n-C_4H_{10}}$. (a) Low pressure region; (b) high pressure region; $\lambda = 334$ nm.

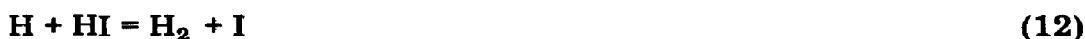
The radicals formed in reactions (1) - (6) either recombine with themselves or add to 1-butene, yielding ultimately a complex spectrum of products.

In our experiments hydrogen iodide will intercept the radicals effectively [10].



The presence of HI results in a simplification of the product spectrum, thus making interpretation of the results much easier. The interpretation is handicapped, however, by the fact that the product of both *n*-butyl and *sec*-butyl radical reaction with HI is *n*-butane.

It should be appreciated that such well-known reactions of hot hydrogen atoms with hydrocarbons as the formation of molecular hydrogen by hydrogen atom abstraction and hydrogen atom substitution are not taken into account. The former removes hot hydrogen atoms from the system and produces 1-butene molecules; the latter leads to hydrogen atom thermalization. Our results do not yield any data concerning the occurrence and importance of these reactions. Thus, the products determined in our experiments originate exclusively from reactions (1) and (2), *i.e.* from the addition of hydrogen atoms to 1-butene irrespective of what happened to these hydrogen atoms before addition. We do not use photochemical quantum yield units ϕ , since some of the hydrogen atoms undergo hydrogen atom abstraction reactions from 1-butene and from HI.



Our value w gives the yield of a product per one hydrogen atom added to butylene, regardless of the position at which the addition occurred.

A mechanism represented by reactions (1) - (11) agrees well with the experimental results. An additional channel for the formation of small amounts of 3-methylheptane may involve addition of *sec*-butyl radicals to the terminal carbon atom in a 1-butene molecule, followed by HI scavenging of octyl radicals; HI may not be 100% effective in scavenging butyl radicals that have a big excess of vibrational energy, far greater than the activation energy for addition to an olefin. Such a decreased effectiveness of HI scavenging has already been reported [11]. However, we cannot exclude that the 3-methylpentane arises from experimental artefacts. Therefore it will not be dealt with any further.

Propylene and methane originate from decomposition of the energized *sec*-butyl radicals (reaction (3)), whereas ethane and ethylene have the excited *n*-butyl radical as a precursor (reaction (5)). Owing to the low conversion and the relatively high HI concentration, undesired side reactions, *e.g.* the reaction of radicals with the molecular iodine formed in reaction (11), apparently do not occur to any appreciable extent, as evidenced by the equality in the yields of propylene and methane, and of ethane and ethylene, respectively.

The results shown in Figs. 1 and 2 clearly indicate the occurrence of competitive processes: dissociation (reactions (3) and (5)) and collisional deactivation (reactions (4) and (6)) of butyl radicals.

Because we experienced difficulties in determining separately the yields for collisional stabilization of *sec*-butyl and *n*-butyl radicals (reactions (4) and (6)), we did not use the following expression of Rabinovitch:

$$S/D = \omega / k_a$$

Rather we chose the familiar Stern-Volmer equation

$$\frac{1}{w_d} = \frac{1}{w_d^0} \left(1 + \frac{\omega}{k_d} \right) \quad (I)$$

where w_d is the amount of decomposition product, w_d^0 is the same amount extrapolated to $p = 0$, k_d is the dissociation rate constant and ω is the collisional frequency.

In this formulation the assumption of strong collisions is inherent; based on this assumption $\omega = 2.09 \times 10^7 p$ (Torr) was calculated. (Lennard-Jones and Stockmayer potential models were used to estimate the necessary collision cross sections [12]. Assuming that the butyl radical is an intermediary between 1-C₄H₈ and *n*-C₄H₁₀ the values of 6.7 and 6.0 Å can be obtained for the pairs C₄H₉-C₄H₈ and C₄H₉-HI respectively.)

The dependence of $1/w_d$ on p is presented in Figs. 3 and 4 for both wavelengths used (334 and 313 nm). For the sake of clarity the relationships for lower (below about 20 Torr) and higher pressures are given separately. At lower pressures the dependence of $1/w$ on p is markedly curved, especially in the case of propylene. At higher pressures, above about 100 Torr, the relationship becomes satisfactorily straight (within the limits of experimental error). Such a course is only to be expected if the butyl radicals have a varying excess of internal energy, *i.e.* if a broad energy spectrum is involved. Since 334 and 313 nm photolyses yield practically monoenergetic hydrogen atoms [13, 14], the butyl radicals formed as a result of the first collision of hydrogen atoms with 1-butene should have a very narrow energy distribution function. (Maxwellian broadening is of no importance in comparison with the enthalpies of reactions (1) and (2) and the energy of hydrogen atoms — see Table 1.) This is obviously not the case. Apparently only some of the hot hydrogen atoms add to the butene in the first collision; the remainder undergo thermalization.

By the trial and error method values for the dissociation rate constants and the corresponding radical yields could be chosen so as to fit the experimental dependence of $1/w_d$ on pressure. The values obtained are shown in Table 2. The calculated values for $1/w_d$ are drawn in Figs. 3 and 4 as solid lines. The data in Table 2 also include the values for the dissociation rate constants of butyl radicals formed in the first collision of hydrogen atoms with 1-butene, calculated using RRKM methods.

The agreement with experimental results is good.

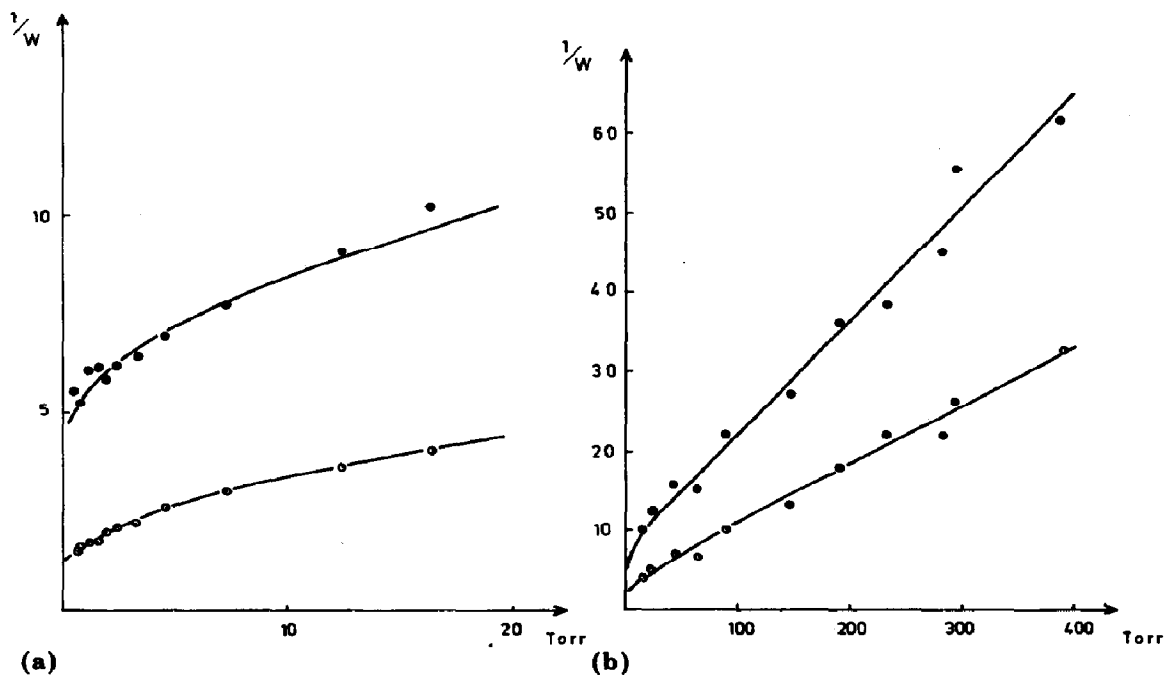


Fig. 3. $1/w_d$ as a function of total pressure for the competitive reactions of dissociation and stabilization of butyl radicals at 334 nm: \circ , C_3H_6 ; \bullet , C_2 hydrocarbons; —, calculated from the data in Table 2. (a) Low pressure region; (b) high pressure region.

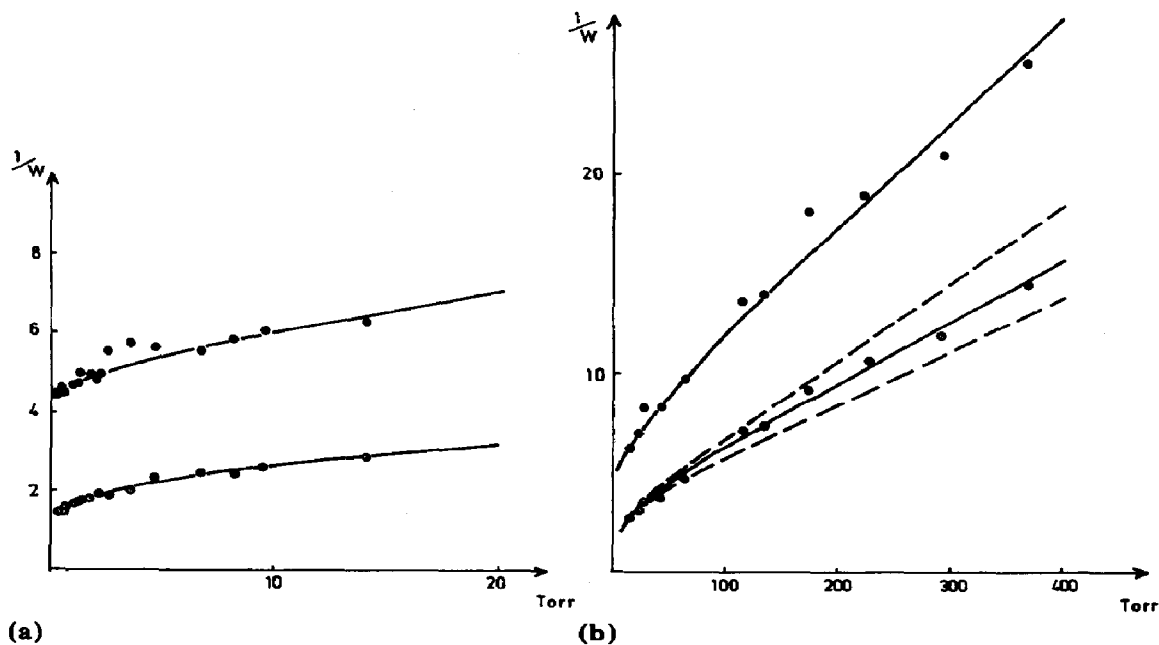


Fig. 4. $1/w_d$ as a function of total pressure for the competitive reactions of dissociation and stabilization of butyl radicals at 313 nm; \circ , C_3H_6 ; \bullet , C_2 hydrocarbons; —, calculated from the data in Table 2. (a) Low pressure region; (b) high pressure region; ---, calculated from the data in Table 2 using $k_d = 2 \times 10^9 s^{-1}$ (upper curve) and $k_d = 3 \times 10^9 s^{-1}$ (lower curve).

TABLE 1

Energies of hydrogen atoms and excitation energies of butyl radicals^a

λ (nm)	E_H	<i>sec</i> -C ₄ H ₉		<i>n</i> -C ₄ H ₉	
		E_{exc}	ϵ^\ddagger	E_{exc}	ϵ^\ddagger
334	15.62 (65.37)	57.3 (239.8)	24.5 (102.5)	53.9 (225.6)	23.9 (100.0)
313	21.35 (89.35)	63.0 (263.7)	30.2 (126.4)	59.6 (249.4)	29.6 (123.8)

^aEnergies given in kilocalories per mole and (in parentheses) in kilojoules per mole. Threshold energies: ϵ_0 (*sec*-C₄H₉) = 32.8 kcal mol⁻¹ (137.2 kJ mol⁻¹) [8]; ϵ_0 (*n*-C₄H₉) = 30.0 kcal mol⁻¹ (125.5 kJ mol⁻¹), calculated from the enthalpy and activation energy for the reaction C₂H₅ + C₂H₄ [14].

TABLE 2

Radical yields and corresponding rate constants for dissociation calculated so as to fit the experimental data

	$\lambda = 334$ nm			$\lambda = 313$ nm		
	<i>Experimental results</i> w	<i>Experimental results</i> k_d (s ⁻¹)	<i>RRKM</i> ^a k_d (s ⁻¹)	<i>Experimental results</i> w	<i>Experimental results</i> k_d (s ⁻¹)	<i>RRKM</i> k_d (s ⁻¹)
<i>sec</i> -C ₄ H ₉ = CH ₃ + C ₃ H ₆	0.25	1.05 × 10 ⁹	9.14 × 10 ⁸	0.25	2.5 × 10 ⁹	2.58 × 10 ⁹
	0.53	4.0 × 10 ⁷		0.25	2.0 × 10 ⁸	
				0.25	2.1 × 10 ⁷	
<i>n</i> -C ₄ H ₉ = C ₂ H ₅ + C ₂ H ₄	0.12	1.2 × 10 ⁹	1.05 × 10 ⁹	0.12	3.2 × 10 ⁹	3.1 × 10 ⁹
	0.10	4.7 × 10 ⁷		0.10	2.6 × 10 ⁸	

^aRRKM calculations were performed based on the thermochemical values given in Table 1.

Three problems should be considered when assessing the value of the data assembled in Table 2.

(1) The assumption of strong collision means that every collision undergone by the activated molecule removes an amount of energy which is sufficient to prevent subsequent decomposition. Although large molecules are thought to be strong colliders, it has been established that excited radicals colliding with molecules such as C₄F₈ and *cis*-2-C₄H₈ lose only 8 - 12 kcal mol⁻¹ (33 - 50 kJ mol⁻¹) in a collision [15, 16]. The energetics of our system are somewhat different; if only such a small amount of energy were to be removed the assumption of strong collision would not be met. Fortunately the magnitude of the high energy decomposition rate constant would not be greatly affected. The decrease in excitation energy by 10 kcal mol⁻¹ lowers the decomposition rate constant by more than an order of magnitude,

as can be assessed using RRKM calculations [6]. Assuming a step-ladder deactivation model the high pressure apparent decomposition rate constant k_a is the sum of rate constants for the individual steps in the cascade:

$$k_a = \sum_{i=1}^n k_i \quad (\text{II})$$

Therefore, under the conditions used in this work the numerical value for k_d would be greater by less than 10% and the highest values for k_d shown in Table 2 would be affected to an even lesser extent.

The occurrence of a cascade would manifest itself by a turn-up of the curve of k_a against S/D at low pressures [17, 18]. The very broad spectrum of radical energies makes it impossible to determine experimentally whether the strong collision assumption is valid.

(2) The assumption that the energy spectrum of radicals consists of sharp bands with corresponding decomposition rate constants is a very rough approximation, especially at lower energies, *i.e.* at lower energies of atomic hydrogen.

We have already suggested that butyl radicals formed in the first encounter of hot hydrogen atoms with butene molecules are, for all practical purposes, monoenergetic. The broadening of the spectrum in the vicinity of the maximum excess energy could occur if primary unreactive collisions of hydrogen atoms with $1\text{-C}_4\text{H}_8$ removed only small amounts of hydrogen atom energy. This should manifest itself by a curvature of $1/w_d$ values at higher pressures, which is unobserved. Therefore, it is assumed that substantial amounts of energy are transferred in unreactive collisions, the energy spectrum of the radicals remaining monoenergetic in this range. This means that thermalization of hot hydrogen atoms in collisions with $1\text{-C}_4\text{H}_8$ and HI molecules occurs according to a step-ladder mechanism, rather than to an exponential mechanism where small energy losses would predominate. After the first unreactive collision hydrogen atoms will cease to be monoenergetic [13]. Thus only high energy values for the decomposition rate constant are meaningful. The curve $1/w_d = f(p)$ is very sensitive to changes in the numerical values of the high energy k_d as can be seen in Fig. 4. The broken lines were calculated for $k_d = 2 \times 10^9 \text{ s}^{-1}$ (the upper curve) and for $k_d = 3 \times 10^9 \text{ s}^{-1}$ (the lower curve). At lower pressures little information concerning the energy distribution of radicals can be gained from $1/w_d = f(p)$.

(3) The values for w , *i.e.* contributions of the radicals with specific k_d , could be used to deduce the real energetic spectrum of hydrogen atoms. Unfortunately reaction (12), the competitive reaction of hydrogen atoms with HI occurs along with reactions (1) and (2). The values of k_{12} differ in magnitude [19 - 21]; for thermal hydrogen atoms $k_{12}/k_{1+2} = 15 - 30$. This ratio is expected to decrease with increasing hydrogen atom energy due to the activation energy of reactions (1) and (2). The occurrence of reaction (12) will deteriorate the spectrum of hydrogen atoms reacting with butene, thus diminishing the contribution of low energy hydrogen atoms. It can only be concluded that less than 35% of the hot hydrogen atoms add to the

double bond; the remainder undergo thermalization. The ratios for the addition of hot hydrogen atoms to the terminal and non-terminal carbon atoms are interesting. It can be deduced from the data in Table 2 that the contribution of the non-terminal addition in the first encounter is about 32%. At lower energies of hydrogen atoms (as assessed based on the corresponding decline of the values for k_d) the contribution of the non-terminal addition decreases to about 16% at $\lambda = 334$ nm. At $\lambda = 313$ nm the decrease is even greater; there is a complete lack (within the limits of experimental and calculated error) of low energy *n*-butyl radicals corresponding to *sec*-butyl radicals that have $k_d = 2.06 \times 10^7 \text{ s}^{-1}$ (this is a value characteristic for the addition of thermal hydrogen atoms [6, 8] — under such conditions the ratio $k_{\text{non-terminal}}:k_{\text{terminal}}$ reported by Falconer and Sunder [22] is about 6%.

Our results confirm the supposition given previously [19], indicating that the small yield for the non-terminal addition is due to the higher activation energy. Steric factors are also likely to be important. The terminal carbon atom in a butene molecule is protected from one side only, whereas access to the non-terminal atom is hindered by two surrounding groups, *i.e.* CH_2 and C_2H_5 . This may explain why no more than 32% of the hot hydrogen atoms add to the internal carbon atom.

5. RRKM calculations of the rate constants for dissociation of excited butyl radicals

In order to establish with more certainty the connection between the observed rate constants for decomposition and the energy of hydrogen atoms we performed some *ad hoc* RRKM calculations by hand (based on Haarhoff's approximation [23]). The vibrational frequencies for butyl radicals were chosen based on those for *n*-butane, using the rules suggested by Rabinovitch and coworkers [6 - 8, 24].

The vibrational frequencies for the activated complex of the *sec*-butyl radical were selected following the treatment of 2-pentyl radicals by Georgakakos *et al.* [18] except that the torsion of bond breaking was lowered fourfold [7] rather than by 60%. For the activated complex of *n*-butyl radicals we chose a somewhat tighter configuration. Such a choice may be reasonable; the values of the pre-exponential Arrhenius factor for the thermal decomposition are a little higher for the *sec*-butyl radicals than for the *n*-butyl radicals, which indicates the greater entropy of activation. For *sec*- C_4H_9 $\log A = 14.8$ [25]; however, this value is probably overestimated [19]. RRKM calculations of Rabinovitch yield a value for $\log A$ of 14.35. For *n*- C_4H_9 $\log A = 13.6$ [26], in good agreement with the rate constant for the reverse reaction, *i.e.* the addition of ethyl radicals to ethylene [19].

The chosen frequencies for the activated complexes are shown in Table 3. Based on them the values for $\log A$ of 13.8 and 14.01 for the *n*-butyl and *sec*-butyl radicals respectively were calculated. These values seem to be reasonable. Also the agreement between the experimental and calculated values

TABLE 3

Frequency changes for the decomposition complex model^a

Radical	Reaction coordinate	C—C → C≡C	Frequency changes	Torsion for forming double bond
1-C ₄ H ₉	950 → 0	950 → 1300	2913(4) → 2986(4)	212 → 400
			1310 → 655	
			1260 → 630	
			346 → 300	
			346 → 173	
			212 → 230	
			102 → 40	
2-C ₄ H ₉	950 → 0	950 → 1300	1450 → 1580	102 → 200
			1310 → 524	
			346 → 435	
			346 → 138	
			212 → 52	

^aAll frequencies are given in reciprocal centimetres.

for the decomposition rate constants is excellent. This confirms the conclusion that dissociation of the radicals formed as a result of the first encounter of hot hydrogen atoms with the butene molecule is indeed observed.

Both our calculations and those of Rabinovitch and coworkers [6 - 8] concerning *sec*-butyl radicals over a broad range of energies agree with each other as well as with the experimental results. This may be regarded as an argument that RRKM calculations can be extended to higher excitation energies.

6. Conclusions

(1) Hot hydrogen atoms add to the double bond of 1-butene but only in part, less than 35%; the remainder undergo thermalization.

(2) Thermalization of hot hydrogen atoms occurs according to a step-ladder mechanism, *i.e.* substantial amounts of energy are transferred in unreactive collisions.

(3) The non-terminal addition is favoured with increasing energy. About 30% of the hot hydrogen atoms add to the inner carbon atom compared with only 5.7% of the thermal hydrogen atoms. Thus highly excited normal radicals can be produced with a good yield.

(4) The use of hot hydrogen atoms extends the range of energies covered by the chemical activation method, making it possible to study the reactions of highly activated radicals.

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