LETERMINATION OF C-C BOND DISSOCIATION EMERGIES IN 1-BUTYME AND 1,2 BUTADIENL

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TABLE OF CONTENTS

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General Considerations	l
Factors Affecting Bond Dissociation Energies	4
Hetnods of Measuring Bond Dissociation Energies	14
A Bond Formation Methods	14
B Bond Fission Methods	15
(a) Photochemical Methods	16
(b) Electron Impact Lethods	19
(c) Thermal methods	24
I Equilibreum Methods	24
II kinetic methods	28
Toluene Carrier Technique	42
Scope of the Fresent Investigation	44
Experimental	48
materials	48
Apparatus	48
Procedure and Analysis	57
1 - Butyne	ó2
Froducts and Results	62
Discussion	68
Mechanism of Decomposition	ပ်ဒီ
Calculation of Activation Energies	70
Fate of the Propargyl Radical	80
Formation of Dibenzyl	82
Thermal Stability of the C3H3Radical	ස්3

TABLE OF CONTENTS (cont)

Hydrogen Froducing Step	84
Conclusions	90
Sample Calculation for Experiment 77	91
l,2 Butadiene	94
Products and Results	94
Discussion	97
mechanism of Decomposition	97
Reactions of the methyl Radicals	97
Fate of the Allenyl Radical	100
Hydrogen Producing Step	101
Formation of Dibenzyl	103
Formation of 1,3 Butadiene	103
Summary of Hechanism	106
kinetic Considerations	106
Calculation of Activation Energies	108
Conclusions	117
General Discussion	118
Calculation of Dissociation Energies	11 8
Stability of the $C_3^H_3$ Radical	122
Conclusions	127
Summary and Contributions to Knowledge	130
Bibliography	134

INDEX TO FIGURES

1.	Graphic representation of bond dissociation energies	
	and ionic covalent resonance	8
2.	Energy vs reaction path co-ordinate	34
3.	Apparatus	49
4.	Reaction vessel	50
5.	Temperature profile along the reaction vessel	52
б.	Analytical section of the apparatus	55
7.	Separation of light hydrocarbons on T.C.P. column of	
	the gas chromatography apparatus	66
8.	Plot of log k _l vs l/T	75
9.	Flot of log k ₂ vs l/T	79
10.	Plot of log kl vs l/T	88
11.	Plot of log k _l vs l/T	113
12.	Flot of log k ₂ vs 1/T	116

1. GENERAL CONSIDERATIONS

Bonds are broken and formed in all chemical reactions. A knowledge of the dissociation energies of the relevant bonds helps one to predict the ease by which a given reaction may take place. It is obvious, therefore, that such information is useful in deciding which reactions should be included in the overall mechanism of a complex system.

The dissociation energy of the bond R_1-R_2 in the molecule R_1R_2 is defined as the endothermicity of the reaction in which the bond R_1-R_2 is ruptured with the formation of two free radicals R_1 and R_2 :-

 $R_1R_2 \rightarrow R_1 + R_2 - D(R_1-R_2)$ kcal/mole.

This change in enthalpy must be computed for the state when R_1R_2 and the products R_1 and R_2 are in the gaseous phase, at zero pressure and at $0^{\circ}K$ (1). Hence the bond dissociation energy defined in this manner is a state property, and its magnitude is determined by the initial and final states without any restriction as to the path of the reaction(s) involved. In practice however, the change in enthalpy at normal temperature is commonly used due to the unavailability of the relevant thermochemical data for extrapolation of \triangle H values to $0^{\circ}K$. In general, the difference between the change in enthalpy at $1000^{\circ}K$ and the bond dissociation energy amounts to about 2 kcal/mole, which is usually within the limits of accuracy of the values obtained

experimentally for bond dissociation energies.

The modern concept of the energy of a chemical bond grew from ideas first introduced by Fajans (2), who proposed that each bond possessed a characteristic and constant energy, independent of its molecular environment. This quantity was called the bond energy, or the bond energy term (3). For a diatomic molecule the bond energy term is obviously equal to the bond dissociation energy, but for polyatomic molecules the situation is more complex.

The sum of the bond energies of all the bonds in a molecule is equal to the heat of atomization of the molecule. For a polyatomic molecule, AX_n , in which there is only one type of bond, the energy of the AX bond was taken as 1/n the heat of atomization. For example, the average energy of the CH bond in methane, obtained from the heat of atomization of methane, is 99.3 kcal/mole (4). Similarly, the OH bond energy, calculated from the heat of formation of water (5), is 110.6 kcal/mole. In molecules with more than one type of bond, the bond energies of all but one type must be known and the energy of the remaining type determined by difference. For example, one value for the CCl bond energy would be the heat of atomization of CH₃Cl minus 3E(CH), the latter being obtained from the heat of methane.

However, currently it is accepted that the energy of a bond varies depending upon its molecular environment. For example, the energy required to remove successive hydrogen atoms from methane is far from constant. The dissociation energies of the first and last CH bonds were measured fairly accurately as 102 kcal/mole (6, 7), and 80 kcal/mole (8), respectively. The dissociation energy of the second CH bond, $D(CH_2-H)$, is rather uncertain, but it appears to be less than 90 kcal/mole (4). Therefore, since the heat of atomization of methane is 392 kcal/mole the C-H bond in the methylene radical is the strongest and amounts to about 120 kcal/mole. The dissociation of H_2O is another example illustrating the effect of molecular environment on bond dissociation energies, thus, D(H-OH) = 117.5 kcal/mole and D(O-H) =101.5 kcal/mole (9).

The concept of bond energy has been reviewed by Szwarc and Evans (10) and discussed at great length by Cottrell (4). It was concluded by these authors that rigorously defined bond energies are in most cases unobtainable, and the former workers suggested that attention be directed to the dissociation energy as the property of more interest to the chemist. The bond dissociation energy is, in principle, a directly measurable quantity, and takes into account all the factors determining the strength of a bond in a particular molecule.

Correlations have been attempted between bond energies and other molecular properties. Noteworthy among these is the relationship of bond energy with bond length (11, 12). Many empirical relations have also been suggested

connecting bond order or multiplicity, polarity, and orbital hybridization with bond length and energy (13). However, the abundance of arbitrary assumptions and hypothesis results in only limited success in the application of these correlations.

Factors Affecting Bond Dissociation Energies

From the definition of the bond dissociation energy, the following relationship is obtained for the process involving the rupture of the bond in the molecule R_1R_2 .

 $\triangle_{H_{f}}(R_{1}R_{2}) = \triangle_{H_{f}}(R_{1}) + \triangle_{H_{f}}(R_{2}) - D(R_{1}-R_{2})$ Consequently factors affecting the heats of formation of the

reactant molecule and of the free radicals produced will affect the bond dissociation energy.

The idea that the dissociation energy of a bond in a particular molecule may be lower by comparison with a standard reference value, when stable fragments were formed, was first suggested by Norrish (14) on the basis of his observations that ketene and azomethane were decomposed by light quanta having less energy than usually required for the dissociation of the bonds being broken. A stable molecule was generated from each of these decompositions and Norrish postulated that due to the release of an energy of "reorganization" when a stable fragment was formed the dissociation energy was lowered.

In the process of bond rupture radicals might be produced which are stabilized by resonance energy. This stabilization energy is ascribed to resonance among several cononical structures. In general the greater the number of structures contributing to the delocalization of the electrons within the radical, the greater is the resonance energy of the radical. Obviously, to put resonance energy on a quantitative basis, a reference standard must be chosen. Szwarc (15) has defined the experimental resonance energy, He, of a radical R as the resultant lowering of the bond dissociation energy in the compound R-X relative to $D(CH_3-X)$ providing the bonds broken are purely covalent. In practice, this definition is applied only to hydrocarbon molecules since only in these molecules can the bonds be considered as purely covalent,

i.e. $R_{e} = D(CH_{3}-H) - D(R-H)$.

The following table of C-H bond dissociation energies collected from values given in reference (4) illustrates the magnitude of the resonance energy of some hydrocarbon radicals:

Hydrocarbon	<u>Dissociation Energy</u>	<u>Resonance Energy</u>
сн ₃ -н	102 kcal/mole	
^C 2 ^H 5 ^{-H}	96 kcal/mole	6 kcal/mole
(CH ₃) ₃ C-H	89 kcal/mole	13 kcal/mole
^С 6 ^Н 5 ^{СН} 2 ^{-Н}	78 kcal/mole	24 kcal/mole
CH ₂ :CH·CH ₂ -H	77 kcal/mole	25 kcal/mole

Opposing this effect is the resonance in the molecule due to participation of ionic structures, such as in halogen derivatives of hydrocarbons, or due to hyperconjugation. For example, in a molecule such as CH₃-X, where

X is a halogen atom, it would be expected that the CH₃-X bond could be represented by a mixture of covalent and ionic structures. Pauling (16) suggested the following empirical relationship

$$\triangle = (D(A-B)) - (D(A-A)D(B-B))^{\frac{1}{2}}$$

where \triangle is the strengthening of the bond between two dissimilar atoms due to ionic covalent resonance. The effect of ionic covalent resonance is exemplified by the following table.

	Str	ength of HA Bonds (1/)	
R	RH	RI	RC1
сн ₃	102	55	81
с ₂ н ₅	96	51	79
^C 3 ^H 7	95	51	77
(CH3)2CH	91	48	
(CH3)3C	89	46	75

The decrease in the RH bond dissociation energy in the series was more marked than with any of the other RX bonds. Baughan, Evans and Polanyi (18) attributed the decrease in the RH bond dissociation energy solely to the increasing resonance energies of the radicals since C-H bonds can be considered as being purely covalent. The strengthening of the bonds in the RX groups was then interpreted as due to the ionic character of the RX bonds and the increased stability of the R^+X^- ion pair in the

molecule. There are thus two opposing factors which influence a bond dissociation energy: the resonance energy of the radical, R_e , which tends to decrease the bond energy, and the ionic covalent resonance energy of the molecule, R_{ic} , which tends to strengthen the bond. If ΔR_{ic} is the difference between the ionic covalent resonance energy of the molecule RX and that of the molecule CH_3X , then

$$D(R-X) = D(CH_3-X) - R_e + \Delta R_{ic}$$

This is best illustrated diagrammatically in Figure 1, page 8, reproduced from the paper of Baughan, Evans and Polanyi (18), which shows the potential energy of the configuration R-X as a function of R-X distance. The curve H_{ii} represents the energy of the purely ionic state of $R^{+}X^{-}$. The curve for only one ionic state, that of $R^{+}X^{-}$ has been shown. The curve for $R^{-}X^{+}$ is not shown since for halides, the energy corresponding to it lies so nigh above the others that its contribution to the energy as a whole is negligible. The curve H_{cc} represents the purely covalent state. Curve E represents the actual state of the molecule CH_3-X (i.e. non resonating radical). H_{cc}^{x} and H_{ij}^{x} represent the energies of the covalent and ionic states respectively when there is resonance in the radical R, and ion R^+ . R_e is the resonance energy of the radical R, R_i is the resonance energy of the R^+ ion. $\Xi^{\mathbf{x}}$ represents the actual state of the molecule RX when there is resonance in the radical R and ion R⁺. It can be seen

Figure 1

Graphic representation of bond dissociation energies and ionic covalent resonance



from this figure, that ionic-covalent resonance causes the ground state to be lower than either the pure ionic or covalent states. The value for $D(CH_3-X)$ shown on the diagram is hence greater than the purely covalent $D(CH_3-X)$ by an amount equal to the ionic-covalent resonance energy, R_{ic} , in the molecule CH_3X . The value for D(R-X) is increased over the value of $D(CH_3-X)$ by the additional co-ionic resonance energy in the molecule RX, AR_{ic} , but is decreased by the resonance energy, R_e , of the radical R.

The magnitude of the ionic-covalent resonance energy in alkyl bromides is computed by comparison of the dissociation energies of the alkyl bromides (19, 20) with the corresponding hydrocarbons:

 $D(CH_3-H) = 102 \text{ kcal/mole}$ $D(CH_3-Br) = 67.5 \text{ kcal/mole}$ $D(C_6H_5CH_2-H) = 78^{\times} \text{ kcal/mole}$ $D(C_6H_5CH_2-Br) = 50.5 \text{ kcal/mole}$

> $\Delta D = 24 \text{ kcal/mole} \qquad \Delta D = 17.5 \text{ kcal/mole}$ $\Delta R_{ic} = 24-17.5 = 6.5 \text{ kcal/mole}$

The C-H bond dissociation energy in toluene is lower than that in methane by the resonance energy of the benzyl radical, R_e , which is 24 kcal/mole. The lowering of the C-Br bond dissociation energy in benzyl bromide with respect to that of methyl bromide is made up of two contributions, namely, the resonance energy of the benzyl radical, R_e , and the increase in ioniccovalent resonance in benzyl bromide, ΔR_{ic} , with respect to methyl bromide. Hence ΔR_{ic} may be taken as 6.5 kcal/mole.

^{*} This value for D(C₆H₅CH₂-H)will be used throughout this thesis, although it has not been definitely established as such (for example, see pages 24 and 31).

Bond energies may also be strengthened by hyperconjugative effects in the parent molecule. For example, neglecting such effects the C-C bond dissociation energy in dibenzyl might be expected to be lower than that for the corresponding bond in ethane by twice the resonance energy of the benzyl radical:

> $D(C_{6}H_{5}CH_{2} - CH_{2}C_{6}H_{5}) = D(CH_{3}-CH_{3}) - 2 R_{e}(C_{6}H_{5}CH_{2})$ = 83 - 2 x 24 = 35 kcal/mole

But from thermodynamic data we have:

$$D(C_{6}H_{5}CH_{2}-CH_{2}-CH_{2}C_{6}H_{5}) = 2\Delta H_{f}(C_{6}H_{5}CH_{2}) - \Delta h_{f}((C_{6}H_{5}CH_{2})_{2})$$

= 47 kcal/mole

The difference in these two values has been explained as the strengthening of this bond in terms of its partial double-bond character caused by the hyperconjugation of the $\widetilde{\mathcal{H}}$ electrons (21). Independent support for this argument has been obtained from measurements of bond lengths by X-ray analysis (22). The length of the C-C bond was found to be 1.48 Å^O, as compared to the normal C-C length of 1.54 Å^O.

Steric factors will also affect the dissociation energy of a particular bond. Thus, the C-C dissociation energy in nexamethylethane, $D(\Phi - C - \Phi)$ is ll kcal/mole whereas $D(CH_3 - CH_3)$ in ethane is 83 kcal/mole. Szwarc (21) pointed out that this discrepancy cannot be attributed to resonance energy of the tripnenylmethyl radicals alone. Steric repulsion between the two bulky groups enhances the lowering of the bond dissociation energy which can be taken as the measured (23) activation energy of 8 kcal/mole required for the recombination of triphenylmethyl radicals. This is due to the compression of the phenyl groups before the C-C bond can be formed.

The inter-relation of bond dissociation energies and internal excitation energy terms have been discussed by Skinner (24) with special reference to the halides of the Group II elements. The following table reproduced from the paper of Skinner (24) shows the relative weakness of the binding in HgX with respect to HgX_2 where X is a halogen atom:

$$\begin{array}{c} \operatorname{Hg} X_{2} \longrightarrow \operatorname{Hg} X + X - D_{1} \\ \operatorname{Hg} X \longrightarrow \operatorname{Hg} + X - D_{2} \end{array}$$

Molecule	D	D ₂	D ₁ - D ₂
HgCl ₂	80.5	24	56.5
HgBr ₂	71.5	16.4	55.1
HgI ₂	57	12	45

In terms of the Heitler-London theory of valence the elements of Group II are zero valent in their atomic ground states¹S, and the formation of a stable covalent type of bond requires an internal excitation of the mercury atom to the divalent state. This energy is probably not less than the energy for the transition $\operatorname{Hg}(6^{1}S_{0}) \longrightarrow \operatorname{Hg}(6^{3}P_{1})$. The bond dissociation energy, D_{2} , would therefore be expected to be lowered by an amount equal to this transition. The actual difference observed is less than this because of contributions of the resonance energies, both ionic and covalent, of the undissociated molecules HgX_2 and HgX.

More recently Carter, Chapel and Warhurst (25) have shown that dissociation of a molecule HgR_2 into three fragments clearly causes a change from the bivalent state to the zero-valent state in the mercury atom. This also occurs when the molecule dissociates into two fragments HgRand R, and hence this reorganization energy is available to help dissociate the second bond. This is responsible for the low values obtained for D_2 in the mercury alkyl compounds.

Quite recently Brown (26) has pointed out that although the measured bond dissociation energy of fluorine is low, the force constant would indicate a strong bond. He postulated that the atoms of fluorine, in the elementary molecule at least, exhibit valence states appreciably different from their ground states, and the bond dissociation energy is lowered by the exothermic term arising from the release of the valence state energy. He suggested that the dissociation energy should be considered as being made up of two terms, i.e. D = BE + RE, where BE is the bond energy i.e. the endothermic separation of the bond components (atoms, radicals, etc.) with retention of the original valence states, and RE is an exothermic reorganization term involving a change of the valence state of an atom (isolated or in a group).

The force constant may be regarded as a direct measure of pG-bond strength in the molecule while the dissociation energy measures the change in both pG and $p\pi$ bonds.

These examples can be taken as special cases of the general effect of "reorganization" energy referred to earlier, which, whatever its source, acts to lower a bond dissociation energy in relation to the standard reference value.

2. METHODS OF MEASURING BOND DISSOCIATION ENERGIES

In a prior section it has been shown that for the process $R_1R_2 \longrightarrow R_1 + R_2$ the bond dissociation energy can be evaluated from thermochemical data, i.e.

 $D(R_1-R_2) = \Delta H_f(R_1) + \Delta H_f(R_2) - \Delta H_f(R_1R_2)$

The heats of formation of stable molecules are usually known or can be calculated from heats of combustion, but unfortunately the knowledge of the heats of formation of free radicals is sparse.

The direct method for measuring the bond dissociation energy is to measure the energy associated with either bond rupture or bond formation. Hence the methods for the determination of bond dissociation energies can be divided into two broad classes: (A) methods in which the process of bond formation is investigated, (B) methods in which the process of bond rupture is investigated.

A. Bond Formation Methods

Generally there are many technical difficulties to overcome in a successful application of this method. To measure the energy liberated in the bond formation process, radicals must first be generated; their concentrations must be measured; and reactions other than recombination must be eliminated. Under ordinary experimental conditions this energy is liberated in the form of heat, hence it must be measured calorimetrically. Obviously this method is best

applicable to the recombination of atoms. Actually, the only successful application of this method was by Bichowsky and Copeland (27) who measured the heat of recombination of hydrogen atoms by direct calorimetry. The hydrogen atoms were produced by an electric discharge; their concentration was estimated by the effusion method; and recombination took place on the palladium surface of the calorimeter which catalyzed the recombination. The value calculated for the dissociation energy of hydrogen was 105 + 3.5 kcal/mole, which is in good agreement with the presently accepted value of 103.2 kcal/mole determined spectroscopically. Copeland (28) attempted similar experiments for the recombination of oxygen atoms. He obtained a value of 165 + 5 for the bond dissociation energy in oxygen which is much higher than the generally accepted value of 117.96 kcal/mole. The possibility of the participation of metastable oxygen atoms in the recombination was not refuted in a decisive way.

B. Bond Fission Methods

Bond fission methods have proved to be more profitable in the determination of bond dissociation energies. This general method can be further divided into subgroups according to the form of energy used to rupture the bond:

- (a) <u>Photochemical Methods</u> in which the energy is supplied in the form of radiation.
- (b) <u>Electron Impact Methods</u> in which the energy is supplied by the kinetic energy of a beam of fast moving electrons,

(c) <u>Thermal Methods</u> in which the energy is supplied in the form of thermal energy. Under this heading the equilibrium and kinetic methods will be differentiated from each other.

(a) Photochemical Methods

Increasing the thermal energy supplied to a group of molecules serves to increase the number of molecules in higher vibrational levels as the energy is equilibrated among all degrees of freedom. Some molecules acquire by this process sufficient vibrational energy necessary to dissociate the weakest bond. Throughout the dissociation process there is no abrupt jump in electronic energy. In contrast, when molecules are subjected to suitable radiation, they can be elevated to electronic states of higher energy. Some of the excited electronic states are unstable; i.e., the interaction between atoms is repulsive at all interatomic distances, and the molecule dissociates. Others of the excited states are stable having a minimum in the energy-interatomic distance curve, but the molecule may be excited to them in such a way that it suffers a sufficient change in vibrational quantum number to cause dissociation. The products of dissociation from an electronically excited state may be atoms in their ground electronic states, but often they are atoms in excited states, or even ions. Hence to determine the bond dissociation energy to ground state atoms, the energies of the following processes must be known, (x denotes an excited atom or molecule, or an ion).

$$AB \longrightarrow (AB)^{\mathbf{x}} \bigtriangleup E_{1}$$

$$(AB)^{\mathbf{x}} \longrightarrow A + B^{\mathbf{x}} \bigtriangleup E_{2}$$

$$B^{\mathbf{x}} \longrightarrow B \qquad \bigtriangleup E_{3}$$

$$D(A-B) = \bigtriangleup E_{1} + \bigtriangleup E_{2} + \bigtriangleup E_{3}$$

Hence for the determination of the dissociation energy the knowledge of the properties of excited or ionized molecules, atoms, and radicals, as well as of normal molecules is required.

Energy differences deduced from the position of certain lines or bands in the spectrum may give quantities directly related to bond dissociation energies. Wavelengths can be measured with great accuracy. Consequently, accurate dissociation energies can be estimated when the experimental data can be treated unambiguously. Unfortunately the results cannot always be interpreted unambiguously due to the complexity of the spectrum. The method is restricted to diatomic molecules since polyatomic molecules give complicated spectra.

The convergence limit of a band spectrum to continuous absorption gives a very accurate measure of the energy required to dissociate the upper state. The best example of the determination of a dissociation energy by this method is that of iodine. The dissociation energy to excited atoms was determined directly from the spectrum. From the approximate heat of dissociation to normal atoms known from thermal data combined with a knowledge of the atomic spectra, the states of the atomic species produced were deduced to be one normal ${}^{2}P_{\frac{1}{2}}$ atom of iodine and one excited ${}^{2}P_{\frac{1}{2}}$ atom of iodine.

Often the continuous spectrum for dissociation represents the dissociation into a normal and excited atom. The excited atom may give off its excitation energy as fluorescence. The long wavelength limit which causes fluorescence corresponds to the upper limit of the dissociation energy concerned. The fluorescence of the excited atom also gives insight as to its state. This method was applied successfully to the alkali halides by Terenin (29).

Birge and Sponer (30) have shown that from spectra which do not show a convergence limit it is possible to calculate the dissociation energy from a plot of the vibrational quanta of the upper state against the vibrational quantum number. The method gives an upper limit for dissociation energies for normal covalent bonds, whereas for ionic molecules it gives a lower limit. Thus, a value of 9.8 ± 0.5 ev. was obtained for $D(N_2)$ by Herman and Herman (31) using this method, which is in good agreement with the currently accepted value of 9.76 ev.

When only continuous spectrum is observed, the long wavelength limit of continuous absorption is a measure of the upper limit to the dissociation energy. The most accurate value for a dissociation energy determined by this method was that of H_2 (32).

As previously stated, there are a large number of electronically excited states possible, although transition to all of them from the ground state may not be allowed by the selection rules or the Franck-Condon principle. Thus, for example predissociation is a phenomenon involving three electronic states: the ground state and two excited states. If the potential energy curve corresponding to one of the electronically excited states, A, to which direct transition is not possible crosses that of another electronically excited state, B, to which transition from the ground state is possible, and if at the level of the crossing point the nuclei have sufficient potential energy to dissociate in the state A, then a radiationless transition from state B to state A may take place, resulting in dissociation. This is characterized by a weakening or disappearance of band structure in the spectrum. The beginning of the diffuseness is known as the predissociation limit which allows the estimation of the upper limit of the bond dissociation energy. However, there are other spectral effects which may be mistaken for pre-dissociations, hence great care is needed in the interpretations of these observations. For example, from a study of the pre-dissociation of CO, the most acceptable value of D(C-O) was found to be ll.l ev. (33).

(b) Electron Impact Methods

Within the last decade a large number of bond dis-

sociation energies have been determined from electron impact studies. In general this method consists of bombarding the molecules under consideration with a beam of electrons which are accelerated across a known potential difference in a mass spectrometer. The beam of electrons having energy much greater than kT are capable of dissociating the molecule into ion fragments, or ion and neutral fragments. By virtue of collisions with these high energy electrons the fragments produced may have excess kinetic energy. In some cases they may also be in electronically excited states.

The minimum energy of the electrons needed to produce an ion in a bond rupture process is defined as the "appearance potential", A_0 . The appearance potential is measured, in principle, by the accelerating potential of the electrons at which a current due to the appropriate ion just appears.

As a result of electron impact three possible types of bond rupture may occur. In the first of these a positive ion and a neutral fragment is generated.

$$AB + e^- \rightarrow A^+ + B + 2e^-$$

For this process the bond dissociation energy, D(A - B), can be related to the appearance potential of the ion A^+ , $A_o(A^+)$, through the following relationship,

 $A_o(A^+) = D(A-B) + I(A) + E_e(A^+) + E_e(B) + E_k(A^+) + E_k(B)$ where I(A) is the ionization energy of A to A^+ , E_e is the electronic excitation energy above the ground state for the fragments, and E_k is the excess kinetic energy of the fragments.

In the second process there is a simultaneous appearance of a positive and negative ion,

$$AB + e^- \rightarrow A^+ + B^- + e^-$$

The relationship between the bond dissociation energy and the appearance potential is the same as shown for the first case except that the electron affinity of B, $E_a(B)$, must be taken into consideration.

$$A_{o}(A^{+}) = A_{o}(B^{-}) = D(A-B) + I(A) - E_{a}(B) + E_{e}(B^{-}) + E_{e}(A^{+}) + E_{k}(A^{+}) + E_{k}(B^{-})$$

The third process involves the capture of an electron.

$$AB + e^{-} \rightarrow A + B^{-}$$
$$A_{o}(B^{-}) = D(A-B) - E_{a}(B) + E_{e}(A) + E_{e}(B^{-}) + E_{k}(A) + E_{k}(B)$$

There are many technical difficulties in obtaining accurate appearance potential measurements. Waldron and Wood (34) lists the operating procedures which tend to keep the errors in appearance potential measurements at a minimum. Field and Franklin (35) feel that with present techniques no appearance potential can be considered as definitely established until several reasonably concordant values have been obtained by different workers.

The ionization potential, I(A), is usually known from the atomic spectrum, if A is an atom. But when A is a free radical, the ionization potential must be determined by direct measurement of $A_{o}(A^{+})$ (= I(A)), when A radicals are introduced into the apparatus.

Frequently there exists several possibilities for the choice of the electronically excited state for an atom, $E_e(B)$, or ion, $E_e(A^+)$, and obviously the value of D(A-B) will depend on it. The assumption that the radicals or radical ions produced from polyatomic molecules are in their ground states is often made, but discrepancies may frequently be due to this assumption. For example McDowell and Warren (36) found D(CN-CN) = 112 kcal/mole. However, Stevenson (37) found this value to be either 159 ± 5 or 106 ± 5 kcal/mole depending on whether the CN radical formed was in its ground states or in the $A^2\pi_1$ state.

Hagstrum (38) has discussed the effect of excess kinetic energy on the value of the appearance potential derived and the conditions under which this effect may arise. The kinetic energy of ions can be determined experimentally by the use of retarding potentials in the mass spectrometer, a detailed discussion of this technique has been given by Hagstrum (38).

There are in general two methods for obtaining bond dissociation energies by means of electron impact studies, i.e. the direct and the indirect methods. In the direct method both the appearance potential and the ionization potential are measured directly. The indirect method was introduced by Stevenson (39). Here the appearance potential of the same ion produced from two different but related molecules are measured and their difference combined with relevant thermochemical data to give the required dissociation energy. For example, the bond dissociation energy of methane, $D(CH_3-h)$, was computed on the basis of the appearance potentials of the $C_2H_5^+$ ion derived from electron impact studies of propane and ethane, and the relevant heats of formation of methane, ethane and propane, and the dissociation energy of hydrogen (39).

$$C_{2}H_{6} + e \longrightarrow C_{2}H_{5}^{+} + H + 2e \qquad A_{0} = 15.20 \text{ ev.}$$

$$C_{3}H_{8} + e \longrightarrow C_{2}H_{5}^{+} + CH_{3} + 2e \qquad A_{0} = 14.50 \text{ ev.}$$

$$C_{2}H_{6} + CH_{4} \longrightarrow C_{3}H_{8} + 2H \qquad \Delta H^{0}_{298} = 5.08 \text{ ev.}$$
By combining these data, the value of $D(CH_{3}-H)$ was computed
as 4.38 ev., in excellent agreement with the value of 4.44 ± 0.2
obtained by Hipple and Stevenson using the direct method (40).
These values for $D(CH_{3}-H)$ are also supported by those derived
from kinetic methods (3), (41).

The exact fragmentation process leading to ionization must be known to calculate bond dissociation energies from electron impact studies, which can be illustrated by means of the following example. Schissler and Stevenson (42) measured the appearance potential of the benzyl radical ion from three different sources, i.e. toluene, ethyl benzene, and dibenzyl. Using these values together with appropriate heats of formation their results led to the value of 8.51 ev. for the ionization potential of the benzyl radical. By contrast, Lossing and associates (43) determined directly the ionization potential of the benzyl radical from several benzyl derivatives as 7.8 ev. In a more recent investigation, Mylander, Myerson

and Grubb (44) indicate that a possible explanation for this discrepancy might be that toluene under electron impact does not yield the benzyl ion but rather the isomeric tropylium Such rearrangements of ions was previously discussed by ion. Rylander and Myerson (45) and even the phenyl ion was considered capable of rearrangement by ring cleavage (46). The precise value of the ionization potential of the benzyl radical is needed for the exact determination of the bond energy in toluene, D(C6H5CH2-H), which is still not definitely established. Nevertheless, Schissler and Stevenson's value of 77 \pm 3 kcal/mole (42) for D(C₆H₅CH₂-H) might still be valid provided that the C_{7}H_{7} ion produced from toluene, etnyl benzene, and dibenzyl in the electron impact studies was the same ionic species containing the same amount of excess energy, if any at The latter estimate agrees well with the value 77.5 ± 1.3 all. kcal/mole obtained earlier by Szwarc (47) by a chemical kinetic method.

(c) Thermal Methods

I. Equilibrium Methods

The determination of the bond dissociation energies by the equilibrium method is based on the measurement of the equilibrium constants for the gaseous reaction:

$$R_1R_2 \leftrightarrow R_1 + R_2$$

where R1 and R2 denote the free radicals produced by the rupture

of the bond in question. From the temperature coefficients of the equilibrium constants, the heat of dissociation can be computed by applying the Van't Hoff isochore, and the recalculation of the heat of dissociation to zero pressure and zero degree Kelvin by definition yields the bond dissociation energy.

The concentration of the free radicals and parent molecule must be measured in the reaction mixture while the equilibrium is maintained. The free radicals produced must not undergo any reactions other than their recombination to regenerate the parent molecule. Unfortunately high temperatures are usually needed to dissociate sufficient amounts of the parent molecule to obtain significantly accurate measurements for the determination of the equilibrium constant. Under these conditions the occurrence of secondary, complicating reactions, i.e. reactions other than recombination, are favoured. hence the method is primarily suitable for estimating the bond dissociation energies of diatomic molecules of the type X_2 , provided additional species sucn as X_3 are not formed.

The most direct application of this method is the static manometric method. A high degree of accuracy was obtained by Perlman and Rollefson (48) in their study of the equilibrium between iodine molecules and iodine atoms, and their value of 35.415 ± 0.050 for D(I-I) compares favourably with the best value obtained by spectroscopic measurements (49).

The extension of this method for the determination of the bond dissociation energies of bromine (50) and chlorine (51) are less reliable, because of the very nigh temperatures needed for appreciable decomposition. A direct method is needed to measure the concentrations of the fragments produced, especially where the extent of dissociation is small. If one of the fragments has an intense colour then colorimetric methods can be used (52), or if the radicals produced are paramagnetic a magnetic method can be used (53, 54). The dissociation of a variety of diatomic molecules composed of metal atoms has been estimated by measuring the changes in the intensity of the absorption bands of these molecules caused by the variation in temperature (55, 56). Polanyi and collaborators developed a very elegant method by the utilization of chemiluminescence for the determination of the bond dissociation energies of sodium (57) and potassium (58). Their method is in effect a variation of the manometric technique using the changes in light intensity as an alternate property to increase in pressure due to the dissociation of the molecules. This method is obviously of restricted applicability.

Bond dissociation energies can also be calculated from thermodynamic data using the following relationship:

 $D(MX) = L_M + \frac{1}{2}D(X_2) + \frac{1}{2}\Delta H_f(X_2,g) - \Delta H_f(MX,s) - L_{MX}$ where L is the heat of vaporization. It is evident that if MA and M are solids, then their heats of vaporization are needed to calculate the bond dissociation energy, since according to the definition of bond dissociation energy parent compound and products must be in the gaseous state. A method to measure the heat of vaporization of metals and metal oxides has been devised using a Anudsen cell by Chupka and co-workers (59). By means of a mass spectrometer, designed to examine the vapour effusing from the small orifice of the Knudson cell, they were able to measure the pressure of the vapour in equilibrium with solid. Using this technique they determined values for the dissociation energies of various metallic oxides (60). There has been much controversy and interest in the past few decades over the heat of sublimation of carbon. Chupka et al (59) determined the composition of the vapour in equilibrium with solid carbon in a Knudson cell at 2500°K. The vapour consisted of C(g), $C_2(g)$ and $C_3(g)$ and the calculated heats of sublimation were found to be 171, 190 and 200 kcal/mole respectively.

Explosion, flame, and detonation methods have been also used to obtain very high temperatures and thus to effect appreciable dissociation. In the adiabatic explosion method the measured final pressure is compared with a calculated final pressure, which is derived from thermochemical data and an assumed value for the unknown bond dissociation energy. The correct choice for the unknown bond dissociation energy will therefore cause no discrepancy between the calculated and observed pressures. Using this technique Lewis and Von Elbe (61) determined the values of 114.6 + 1 and 104.3 + 1 kcal/mole for the bond dissociation energies in water, D(H-OH) and D(O-H) respectively. These estimates do not agree too well with the currently accepted values of 118.5 ± 0.7 and 100.4 + 0.9 kcal/mole respectively (62). In the flame method the flame temperature is compared with the calculated flame temperature. Gaydon and co-workers (63) applied this method for a cyanogen-oxygen flame. Their results showed best agreement when $D(N_2)$ was chosen to be 9.76 ev. Measurements of detonation velocity, which depends on the energy released in a shock wave, have been used to determine the dissociation energies of CO, CN, and N_2 by Kistiakowsky and co-workers (64) in a cyanogen-oxygen system. Reliable thermodynamic data were available for all the reactions concerned except the dissociation of carbon monoxide, nitrogen and cyanogen. Their measurements were compared with calculations made assuming the various disputed dissociation energies for these molecules. The best agreement was obtained with $D(N_2) = 9.76 \text{ ev.}, D(CO) = 11.11 \text{ ev.}$ and D(CN) = 7.6 ev; and their results could not be reconciled with the lower values of these molecules. This set of results was the first in a series of studies by various methods supporting the high values for the dissociation energies of nitrogen and carbon monoxide, which are now generally accepted.

II. Kinetic Methods

The dissociation of polyatomic molecules usually leads to the formation of free radicals which are capable of undergoing fast, secondary reactions with the parent compound or the products. Consequently equilibrium methods are usually not applicable for estimating the dissociation energies of such molecules.

For a chemical reaction involving the rupture and formation of bonds the heat of reaction is equal to the sum of the dissociation energies of the bonds broken minus the sum of the dissociation energies of the bonds formed:

 $\Delta H = \sum D$ (bonds broken) $-\sum D$ (bonds formed). In turn, the heat of reaction, ΔH , is equal to the difference between the activation energies of the forward and reverse processes respectively:

$$\Delta H = E_{f} - E_{r}$$

The activation energies for the forward and reverse processes can be obtained in principle from the temperature coefficients of the corresponding rate constants, k_f and k_r .

Using this relationship, Kistiakowsky and co-workers were able to deduce the values of a number of C-H bond dissociation energies on the basis of the activation energies for the steps

$$Br + RH \xrightarrow{k_f} R + HBr$$

 k_r

derived from their study of kinetics of the thermal and photochemical bromination of hydrocarbons (65, 66). This method can best be illustrated by using their study of the photobromination of methane as an example (65). The rate of disappearance of browine was measured photometrically to establish the kinetics of the reaction. The initial rate of disappearance of promine was expressed by the relation:

$$- \begin{bmatrix} \frac{d(Br_2)}{dt} \end{bmatrix} = k'(CH_4)(br_2)^{\frac{1}{2}}(1/F)^{\frac{1}{2}}$$

t=0

where F is the total pressure of the reactants. The following scheme was postulated to conform with this expression.

$$Br_2 + hY \longrightarrow Br + Br$$
 (1)

$$Br + CH_4 \longrightarrow CH_3 + HBr$$
 (2)

$$\operatorname{GH}_3 + \operatorname{Br}_2 \xrightarrow{} \operatorname{GH}_3 \operatorname{Br} + \operatorname{Sr}$$
 (3)

$$CH_3 + HBr \longrightarrow CH_4 + Br$$
 (4)

$$Br + Br + M \longrightarrow Br_2 + M \tag{5}$$

applying the steady state method, this scheme leads to the more explicit expression:

$$-\frac{d(Br_2)}{dt} = \frac{d(H_3Br)}{dt} = \frac{k_2k(I)^{\frac{1}{2}}(OH_4)(Br_2)^{\frac{1}{2}}(I/F)^{\frac{1}{2}}}{1+k_4}$$
$$\frac{HBr}{HBr}$$

where I is the light intensity, and k is a non-temperature dependent apparatus constant. The required dependence on the square root of the light intensity, and the inhibition by hBr were demonstrated experimentally. A plot of log k' acainst 1/Tgave a straight line, the slope of which led to a value of 17.8 kcal/mole for the activation energy. This temperature dependence of the rate constant was ascribed to reaction (2), i.e. $E_2 = 17.8$ kcal/mole. From the temperature dependence of the inhibition by hydrogen bromide the difference in activation energies
between reactions (3) and (4) was calculated to be 2 kcal/mole i.e. $E_4 - E_3 = 2$ kcal/mole. On the supposition that reaction (3) was highly exothermic they postulated that its activation energy was zero. Therefore, a value of 2 kcal/mole was assigned to E_4 which is in good agreement with the value of 1.5 kcal/ mole estimated by Anderson and Nistiakowsky (41) from experiments on the photolysis of methyliodide in the presence of hydrogen bromide. Thus the difference, $E_f - E_r$, for the reaction between bromine atoms and methane, is 17.8 - 1.5 kcal/mole \simeq 10.3 kcal/mole. From this result, and the value of D(H-Br), the value of D(OH₃-h) was calculated as 103 kcal/mole at 450° K or 101 kcal/mole at 0° K.

Similar studies with other hydrocarbons yielded values which agreed well with those obtained by other methods, with the exception of toluene (67). A value of 39.5 Kcal/mole was suggested by Anderson, Scheraga and Van Artsdalen for $D(C_6H_5OH_2-H)$, whereas other methods have yielded values of about 78 kcal/mole (42,47). The photobromination of toluene was assumed to follow the same pattern as the photobromination of methane. The assumption that $E_3 = 0$ was again made.

The reaction of a methyl radical with bromine is indeed exothermic to the extent of 22 kcal/mole, this value representing the difference $D(Br_2) - D(GH_3-Br)^{\texttt{X}}$. Therefore

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[×] $\Delta h = \Sigma D$ (bonds broken) - ΣD (bonds formed) $D(CH_3-Br) = 67.5$ kcal/mole (68), $D(C \cap CH_3-Br) =$ 50.5³kcal/mole (69), $D(Br_2) = 45$ kcal/mole (17)

the assumption that the activation energy of reaction (3) in the photobromination of methane seems justifiable. However, the exothermicity of the reaction of a benzyl radical with bromine is given by the difference $D(Br_2) - D(C_6H_5CH_2-Br)^*$, which is only about 5 kcal/mole and therefore one would expect that this reaction is associated with some activation energy. Hence, the value for $D(C_6H_5CH_2-H)$ should be lower than 89.5 kcal/mole by whatever activation energy might be required for reaction (3). From the studies of analogous reactions (70) one may reasonably suggest that the activation energy for the reaction of benzyl radicals with bromine might be of the order of 6 - 7 kcal/mole, and hence $D(C_6H_5CH_2-H)$ would not be higher than 82 kcal/mole.

The activation energy for the dissociation of a molecule into two radicals will equal the endothermicity of the reaction if the activation energy for the recombination of the radicals is zero. On the basis of this assumption the measured activation energy for the reaction involving the rupture of one bond would be equal to the dissociation energy of the bond.

Szwarc (1) has demonstrated on the basis of the theory of absolute reaction rates that there is a close agreement between the experimental activation energy of a unimolecular reaction involving the dissociation of one bond only and the bond dissociation energy. He pointed out, however, that there was some difficulty in defining the transition state complex for a unimolecular dissociation, and distinguished between two types of decomposition:

- (1) Decompositions leading to the formation of two stable products, the recombination of which involves an activation energy, e.g. $C_2H_5Br \rightarrow C_2H_4$ + HBr
- (2) Decompositions leading to the formation of two radicals, recombination of which requires no activation energy,
 e.g. C₂H₅Br → C₂H₅ + Br ·

In the dissociation process of the first type there is no difficulty encountered in the definition of the transition state complex. A plot of the energy of the system as a function of the reaction path co-ordinate is shown in Fig. (2a). The hump of this curve represents the transition state which is, therefore, completely defined by the co-ordinates of this point. Fig. (2b), on the other hand, illustrates a decomposition of the second type, and because it does not show a hump a similar interpretation of the transition state complex is impossible. In order to avoid difficulties arising from the absence of description of the transition state complex, Szwarc adopted for the latter case a slightly modified treatment of the transition state method, the outline of which is given below.

All the energy levels corresponding to various modes of some particular bond in some particular molecule can be Figure 2

-

Energy $\underline{vs}.$ reaction path co-ordinate





classified into two groups:

- Energy levels which correspond to vibrations of the bond, i.e. for which the energy is smaller than the bond dissociation energy D.
- (2) Energy levels which correspond to the translational modes of motion, i.e. for which the energy is greater than D.

These two groups of energy levels are denoted by A and B in Fig. (2b); it is obvious that a particular bond will be broken only if it is in a state which corresponds to Class B. If we assume that there is no interaction between energy levels corresponding to various degrees of freedom, the total partition function of the molecule can be represented by

$f_{total} = f' \cdot f_k$

where $f' = \mathcal{H}' f_i$ and represents the product of all the partition functions for all i values with the exception of i = k, and f_k represents the partition function corresponding to the vibrational degree of freedom of the bond to be broken. The partition function f_k can be represented by

$$f_{k} = \sum e^{-\xi_{j/kT}} + e^{-D/kT} \cdot f_{transl}$$

$$\simeq \sum e^{-\xi_{j/kT}}$$

the summation being taken over all the vibrational energy levels, the jth of them corresponding to the energy \mathcal{E}_{j} , taking $\mathcal{E}_{o} = 0$. D is the dissociation energy of the bond in question, i.e. the difference between the vibrational zero energy level

and the convergence limit of the vibrational levels, and $f_{transl.}$ denotes the partition functions of translational levels belonging to Class B and measured from the energy level of the convergence limit taken as zero.

If it is assumed that the "centre of gravity" of the bond in question is restricted to some se_{em} ent <u>ds</u> along the direction of the bond, then the partition function for f_{transl} . may be represented as

i.e. as for a "particle in a box". The fraction of the molecules which contain the requisite amount of energy in the bond to be broken and for which the centre of gravity of this bond is confined to the segment ds is given by

$$\frac{1}{N} = \frac{N}{N} \frac{1}{N} \frac{$$

i.e.
$$\frac{\pi^{1}}{n} = \frac{(\pi^{1}f_{i})e^{-D/kT}(2\pi u_{kT})^{\frac{1}{2}}h^{-1}ds}{(\pi^{1}f_{i})(\sum_{e} -\varepsilon_{j/kT} + e^{-D/kT}f_{transl.})}$$

This expression is further simplified if it is assumed that energy levels \mathcal{E}_j correspond to a harmonic oscillator. Then, $\sum_{e} - \mathcal{E}_j / kT \simeq (1 - e^{-hY_0/kT})^{-1}$

where Y_0 denotes the fundamental vibration of the bond in question. If it is assumed further that half the number of molecules which can decompose are moving in the direction of decomposition with an average thermal velocity $\left(\frac{(2kT)}{\widetilde{n}\mathcal{U}}\right)^{\frac{1}{2}}$, then

the rate constant k_u for the decomposition is given by the number of these molecules for which the centre of gravity will pass the segment <u>ds</u> in unit time,

i.e.
$$\frac{1}{2} (2\pi \mu kT)^{\frac{1}{2}} (1 - e^{-hYo/kT})h^{-1}e^{-D/kT} \frac{ds}{ds} \left(\frac{2kT}{\pi \mu} \right)^{\frac{1}{2}} \frac{1}{ds}$$

which is reduced to

$$k_u = \frac{kT}{h} (1 - e^{-h ro/kT}) e^{-D/kT}$$

We can now distinguish between two extreme cases:

(1) $h \Upsilon_{o} \langle \langle kT \rangle$ (2) $h \Upsilon_{o} \rangle kT$

For case (1) $(1 - e^{-h\Gamma o/kT}) \simeq hYo/kT$ and the expression for the rate constant reduces to

$$k_u = \gamma_0 e^{-D/kT}$$

we can write, therefore,

$$\frac{RT^{2}}{\partial T} = \frac{D}{kT^{2}} \cdot RT^{2} = ND = D$$

where N is the Avogadro number, and D the dissociation energy in kilocalories per mole. The L.H.S. of this expression is the Arrhenius activation energy usually referred to as the "experimental" activation energy. Therefore, for this case the experimental activation energy of a unimolecular dissociation process is precisely equal to the dissociation energy of the ruptured bond. The expression derived for the rate constant of a unimolecular dissociation demands that the frequency factor should be nearly equal to the fundamental vibration frequency of the bond in question, which is about $10^{12}-10^{13}$ sec⁻¹ (49). Hence the theoretical treatment predicts the expected value of the frequency factor.

For case (2), the term (1 - $e^{-hYo/kT}$) ~ 1 and the expression for the rate constant is reduced to

$$k_u = \frac{kT}{h} \cdot e^{-D/kT}$$

The experimental activation energy measured by $RT \frac{2 J_{lnk_u}}{3T}$ is given now by

 $E_{exp} = RT + D$

and, therefore, at 1000° K the experimental activation energy gives results which are too high by about 2 kcal/mole. The frequency factor in this case is given by $\frac{kT}{b}$ which for T

= 500° K is approximately equal to 10^{13} sec⁻¹. Here again, the theoretical treatment predicts a value for the frequency factor which agrees well with the fundamental vibration frequency of the bond. In a recent review article by Gowenlock (71), frequency factors for unimolecular reaction were considered "normal" if they were in the range $10^{11.5} - 10^{14.5}$ sec⁻¹. It was felt that when reactions have frequency factors smaller than $10^{11.5}$ sec⁻¹ might be attributed to either restriction of motion in the transition state, or a low transmission coefficient due to the participation of a "forbidden" transition in the rate determining step. Reactions that possess large frequency factors (greater than $10^{14.5}$ sec⁻¹) may involve either a "loose" transition state, or a decomposition into three or four fragments due to the "spread" of the activation energy into more than one bond.

There are many experimental problems in the determination of the rate of initial decomposition. Experimentation is limited to the type of decomposition in which the weakest bond of the molecule is ruptured, and it is desirable, therefore, that this bond should be considerably weaker than any other bond in the molecule. The primary dissociation is usually followed by the subsequent reactions of the radicals formed. Hence numerous complications may obscure the kinetics of the decomposition and may make their interpretation ambiguous. Ideally a system should be chosen in which the generated free radicals are either removed irreversibly, before reacting with the undecomposed molecules, or their concentrations measured before they can react.

The C-I bond dissociation energies of various organic iodides were estimated Butler and Polanyi (3), and Butler, Mandel, Mandel (72) who investigated the rate of pyrolysis of a series of organic iodides in a flow system. They employed a flow system in order to reduce the time of reaction to a fraction of a second, limiting the decomposition to a small percentage and thus minimizing the chances of secondary reactions. This method has the added advantage that the products can be accumulated over extended periods of time. Since the C-I bond is the weakest bond in organic iodides, it is obvious that the first step in the pyrolysis of these compounds involves the rupture of this bond in preference to any other, i.e. $RI \longrightarrow R + I$. The rate of the initial decomposition was considered to be approximately equal to the rate of formation of iodine resulting from the dimerization of iodine atoms. The latter step was assumed to occur by three body collisions in the gas phase or on the wall of the reaction vessel. They assumed that the reverse reaction was negligible and that the R radicals did not initiate a chain reaction, and, therefore, identified the rate of formation of iodine with the initial rate of decomposition. For many iodides these assumptions were plausible and the derived bond dissociation energy agreed well with those obtained later by other methods (7, 41).

In spite of the fast flow used in this system many complications could not be completely prevented. For example the organic radicals might react with iodine molecules or recombine with I atoms. Furthermore, the organic iodide might decompose by a molecular mechanism, splitting out hydrogen iodide. Butler and Polanyi concluded that in some cases the activation energies calculated from the temperature coefficient of the rate constant were not reliable. Instead, they assumed a value of 10^{13} sec⁻¹ for the frequency factor in the Arrhenius equation and calculated the activation energy from the rate constants at the lowest temperature, where the smallest extent of decomposition had occurred. In many cases their results agree well with currently accepted values.

Szwarc extended this technique to the study of the

pyrolysis of toluene (47). He employed a fast flow system with a short time of contact such that the amount of decomposition was low. The study was conducted in the temperature range of 680-850°C and over a pressure range of 2 - 15 mm hg. To explain his experimental data he postulated the following mechanism.

$$C_{6}^{H}C_{6}^{H}C_{6}^{H}C_{2}^{\bullet} + h.$$
(1)

$$H_{\bullet} + c_{0}^{h_{5}}CH_{3} \longrightarrow H_{2} + c_{0}^{h_{5}}CH_{2}.$$
 (2)

$$H_{\bullet} + C_{o^{n}5}CH_{3} \longrightarrow C_{6}C_{6}C_{6} + CH_{3}.$$
(3)

$$CH_3. + C_0H_5CH_3 \longrightarrow CH_4 + C_0H_5CH_2.$$
(4)

$$2 \circ_{6} H_{5} OH_{2} \longrightarrow (\circ_{6} H_{5} OH_{2})_{2}$$

$$(5)$$

We concluded that the rate-determining step was reaction (1) and that its rate was measured by the rate of formation of hydrogen plus methane. Moreover, he found that the decomposition was a nonogeneous, first-order reaction with an activation energy of 77.5 ± 1.3 kcal/mole. The frequency factor was found to be 2 x 10^{13}sec^{-1} . Making the usual assumption that the recombination of radicals requires no activation energy[#], Szwarc identified this activation energy with the C-H bond dissociation energy in toluene, i.e. $D(G_{6}n_{5}Cn_{2}-n) =$ 77.5 ± 1.3 kcal/mole. Similarly, Szwarc and associates showed that the pyrolysis of a series of compounds related to toluene such as p-, m- and o- hylenes (73), p-, m- and o- fluorotoluenes $(74), \mathbf{a} - \mathbf{\beta} - \text{and } \mathbf{y}$ picolines (75) could be represented by a similar mechanism to that of toluene.

^{*} This contention is supported by the recent results of rebarle and Avrahami (97) that the recombination of allyl radicals, which are stabilized to the extent of 25 kcal/mole, does not require any activation energy.

The Toluene Carrier Technique

From these studies evolved the toluene carrier technique which has been widely used for the determination of bond dissociation energies. Since toluene possesses a relatively weak C-H bond, Szwarc expected that toluene would serve as an efficient radical scavenger, with the added advantage that the benzyl radical formed would be unreactive and thermally stable. Thus, if a molecule R_1R_2 is decomposed into radicals R_1 and R_2 in the presence of an excess of toluene, these radicals, if sufficiently reactive, might rapidly abstract a hydrogen atom from toluene to form stable products, and the benzyl radicals thus formed would eventually dimerize to dibenzyl.

According to this mechanism the initial dissociation of R_1R_2 can be identified with the rate of formation of dibenzyl, which in turn would be expected to be equal to the rate of formation of R_1H or of R_2H .

For a successful application of this method a flow system with a short time of reaction is used to minimize reactions of the radicals with the products or the starting material. Furthermore, the radicals produced must be sufficiently reactive to abstract a hydrogen atom rapidly from toluene. This process is favoured by maintaining a high ratio of toluene to reactant. The activation energy of the overall reaction may be identified with the bond dissociation energy only if the decomposition has been established to be a unimolecular, homogeneous, first-order, dissociation reaction. The method is primarily limited to the determination of dissociation energies less than $D(C_6H_5CH_2-H)$ and Szwarc (76) has recommended that for best results the dissociation energy be at least 10 kcal/mole smaller than that of toluene.

Many classes of compounds have been pyrolyzed using the toluene carrier technique. Compounds of the type benzyl-R where R is a reactive radical lend themselves most suitably for such a study. Since the dissociation energy of the benzyl-R bond is considerably weakened by the large resonance stabilization of the benzyl radical (see page 5), it is usually the weakest bond in the molecule. The dissociation step yields the radical R with few complicating reactions. The heat of formation of this radical can then be obtained if the heat of formation of the compound is known using the measured bond dissociation energy. The study of benzyl bromide (20) serves as an example of this type of study. Similar mechanisms to that postulated for benzyl bromide have been shown to nold for the decomposition of many compounds, e.g. allyl bromide (20), substituted benzyl bromides (77), n-propyl benzene (78), benzylamine (79), ethyl benzene (80) and 1-butene (81).

The Scope of the Fresent Investigation

The C_3H_3 radical can be represented by at least the two canonical structures, i.e. that of the propargyl radical, $CH=C-CH_2$, and that of the allenyl radical, $CH_2=C=CH$. Hence one would anticipate that the C_3H_3 radical would have a considerable resonance energy and that in consequence the corresponding C-C bond dissociation energies in 1-butyne, $D(CH:C+CH_2-CH_3)$, and 1,2 butadiene, $D(CH_2:C:CH-CH_3)$, would be substantially lowered with respect to the value of $D(CH_3-CH_3)$. Acreover, these C-C bonds would be expected to be the weakest in the respective molecules. If indeed the C_3H_3 radical generated from 1,2 butadiene and 1-butyne assumes the same configuration(s) then the difference in the two corresponding C-C bond dissociation energies would be simply equal to the difference between the heats of formation of 1,2 butadiene and 1-butyne:

$$\begin{split} \mathsf{D}(\mathsf{CH}_2:\mathsf{C}:\mathsf{CH}-\mathsf{CH}_3) &= \mathsf{D}_a = \Delta \mathsf{H}_f(\mathsf{C}_3\mathsf{H}_3) + \Delta \mathsf{H}_f(\mathsf{CH}_3) - \Delta \mathsf{H}_f(\mathsf{CH}_2:\mathsf{C}:\mathsf{CH}\cdot\mathsf{CH}_3) \\ \mathsf{D}(\mathsf{CH}:\mathsf{C}\cdot\mathsf{CH}_2-\mathsf{CH}_3) &= \mathsf{D}_b = \Delta \mathsf{H}_f(\mathsf{C}_3\mathsf{H}_3) + \Delta \mathsf{H}_f(\mathsf{CH}_3) - \Delta \mathsf{H}_f(\mathsf{CH}:\mathsf{C}\cdot\mathsf{CH}_2\cdot\mathsf{CH}_3) \end{split}$$

$$\Delta D = D_a - D_b = \Delta H_f (CH: C \cdot CH_2 \cdot CH_3) - \Delta H_f (CH_2: C: CH \cdot CH_3)$$
$$= 0.71 \text{ kcal/mole}^{\texttt{x}}$$

 $\Delta H_{f}(CH_{2}:C:CH \cdot CH_{3}) = 38.77 \text{ kcal/mole}, \Delta H_{f}(CH_{2}:C:CH_{2} \cdot CH_{3})$ = 39.48 kcal/mole (82).

From a survey of the literature it would appear that only a limited amount of work has been done on the C_3H_3 radical. Collin and Lossing (83) showed that C_3H_3 radicals were produced in the mercury photosensitized decompositions of allene, 1,2 butadiene and 1,3 butadiene. The C_3H_3 radicals formed from allene and 1,3 butadiene were shown to combine with methyl radicals to give mainly 1-butyne. On this basis they favoured the propargyl structure for the C_3H_3 radical. Hecently Srinivasan (84) studied the photochemical decomposition of 1,3 butadiene and reported that C_3H_3 radicals were produced. In the latter study two different products with a mass corresponding to C_6H_6 were found and in consequence Srinivasan suggested that the C_3H_3 radical might react in both the propargyl and allenyl configurations.

There is some controversy as to the correct values for the C-C bond dissociation energies in 1-butyne and 1,2 butadiene. Collin and Lossing (85) measured the appearance potentials of the $C_3H_3^+$ ion produced from allene, propyne, 1-butyne, 1,2 butadiene and 1,3 butadiene on electron impact. The heat of formation of the $C_3H_3^+$ ion was calculated from these measurements and the relevant thermochemical data. For example, for the reaction

 $CH: C \cdot CH_2 \cdot CH_3 + e \rightarrow CH: C \cdot CH_2^+ + CH_3 + 2e$ the following relation was used

 $A_0(C_3H_3^+) = \Delta H_f(C_3H_3^+) + \Delta H_f(CH_3) - \Delta H_f(CH_2 \cdot CH_2 \cdot CH_3)$ Since there was little discrepancy in the values calculated for

the heats of formation of the $C_3H_3^+$ ion, they assumed that the $C_3H_3^+$ ion derived from each of these compounds was identical. From a consideration of the values calculated by Coats and Anderson (86), using group contributions, for the heats of formation of all possible configurations for the $C_3H_3^+$ ion, Collin and Lossing concluded that the $C_3H_3^+$ ion had the propargyl configuration. The difference between the average value obtained for the heat of formation of the $C_3H_3^+$ ion and the ionization potential of the propargyl radical, directly determined previously by Farmer and Lossing (87), represents the heat of formation of the $\rm C_3H_3$ radical, which was calculated as 75 kcal/mole. From this value together with the relevant thermochemical data the C-C bond dissociation energies in 1-butyne and 1,2 butadiene were calculated as 67.5 and 68.2 kcal/mole respectively. On the other hand, Coats and Anderson (86) derived a value of 59 kcal/mole for D(CH:C·CH2-CH3) from measurements of the appearance potential of the $C_3H_3^+$ ion from 1-butyne and the ionization potential of the $C_3H_3^+$ ion measured directly by Farmer and Lossing (87). However, Coats and Anderson pointed out that calculations based on their appearance potential measurements may be in error by as much as 10-12 kcal/mole. If indeed the $C_3H_3^+$ ions generated from allene, propyne, 1-butyne, 1,2 butadiene and 1,3 butadiene were the same ionic species, then the results of Collin and Lossing may be considered more reliable since they were computed using an average value for the heat of formation of the

 $C_3H_3^+$ ion produced from different sources.

In view of the discrepancy between the values of Collin and Lossing and those of Coats and Anderson, the present investigation was undertaken to determine the bond dissociation energies in 1-butyne and 1,2 butadiene by means of the toluene carrier technique. It was anticipated that this study would resolve this lack of agreement and would thus establish a more definitive value for the heat of formation and the resonance energy of the ${\rm C}_{3}{\rm H}_{3}$ radical. The present investigation is analogous to the study of the pyrolysis of 1-butene made by Sehon and Szwarc (81). According to these workers the primary step in the decomposition of 1-butene yielded a CH_3 and an allyl radical. The C-C bond dissociation energy in 1-butene was calculated at 61.5 kcal/ mole and in conjunction with relevant thermochemical data it was concluded that the allyl radical was stabilized by resonance energy to the extent of about 25 kcal/mole. Un the assumption that the mechanism of pyrolysis for 1-butyne as well as for 1,2 butadiene was similar to that of 1-butene, it was anticipated (i) that these two compounds would yield on decomposition a CH_3 and a stable C_3H_3 radical, and (ii) that the rate of rupture of the appropriate C-C bond could be measured by the rate of formation of methane or the products resulting from the C3H3 radical. Furthermore, it was expected that from an analysis of the latter products, some information regarding the chemical properties of the $C_{3}H_{3}$ radical would be gained.

EXPERIMENTAL

materials

Research grade 1-butyne was obtained in a metal cylinder from Farchan Co., Cleveland, Ohio. It was further purified by repeated vacuum distillation, which ensured the removal of any traces of permanent gases. A sample of 1-butyne was analyzed by vapour phase chromatography, which will be described in detail in a later section. No impurities were detected by this method.

The 1,2 butadiene was generously supplied by Polymer Corporation, Sarnia, Ontario. The 1,2 butadiene was purified and tested in the same manner as 1-butyne. Again, no impurities were detected.

Nitration grade toluene was generously supplied by Gulf Petroleum Co., Pittsburgh, Pa. The toluene was dried and distilled through an efficient column and the fraction boiling at 110.5°C was collected.

Apparatus

The pyrolysis was studied in a high vacuum flow system shown in Fig. 3 page 49.

The reaction vessel, R, shown in greater detail in Fig. 4 page 50, was entirely of quartz and was joined to the rest of the apparatus with graded quartz to pyrex seals. The long thermocouple well permitted the measurement of the temperature along the length of the reaction vessel. The time

<u>Figure 3</u> Apparatus



Figure 4

Reaction Vessel



spent by the gas in sections A and C was small compared to section B, hence there was negligible decomposition in these sections. The temperature in the reaction vessel was measured by means of a chromel-alumel thermocouple using an ice-water mixture at the cold junction. The thermocouple was periodically checked against a standard chromel-alumel thermocouple (calibrated by Thermo Electric Co. Inc., Fairlawn, N.J.) and the voltage was measured with a Leeds and Northrup K_2 -potentiominter. A typical temperature profile along the reaction vessel is shown in Fig. 5 page 52. As can be seen from this diagram the temperature along section B was practically uniform, and the temperature gradient fell sharply across sections A and C, thus minimizing again any reaction occurring in the latter sections.

The effect of the surface of the reaction vessel on the reaction was examined by using a similar reaction vessel, section B of which was packed with quartz wool. (The quartz wool was obtained from Micro Chemical Specialities, Berkley, Galif.). The average diameter of the fibres used was 3×10^{-3} cm. and their average length was about 15 cm. The weight per fibre was about 3×10^{-4} gm. and about 6.2 gm. were used for the packing. The surface area of one fibre was about 0.15 cm² so that the total surface area of the packing was about 3100 cm^2 . The radius of the reaction vessel was 18 mm. and the total surface area therefore, about 230 cm². The surface/ Figure 5

Temperature profile along the

reaction vessel



volume ratio of the unpacked vessel was thus about 1.1 cm⁻¹, while that of the packed vessel about 15.1 cm⁻¹. The surface/ volume ratio was therefore increased by a factor of about 14 in the packed reaction vessel.

The reaction vessel was inserted in an inconel tube which provided for equalization of temperature. The inconel tube, in turn, was inserted in a furnace H (Fig. 3) consisting of a nichrome wire wound on a refractory tube. (The refractory tube was purchased from Norton Co., Worcester, Mass. and was provided with a groove). The nichrome wire was divided in 5 sections to allow for adjustment of the temperature gradient along the reaction vessel. The furnace was thoroughly insulated with rockwool contained in a metal drum of diameter 23 in. and length 2 ft. The temperature was kept constant within $\pm 2^{\circ}$ C by a temperature regulator purchased from the Thermo Electric Co. Inc., Fairlawn, N.J. The sensing element of the regulator was an independent thermocouple inserted in the thermocouple well of the furnace.

The toluene was introduced from a 100 ml. round bottom flask, F, through a short, internally sealed capillary C_1 . During an experiment the toluene flask was immersed in water in a 5 l Dewar vessel, D, maintained at constant temperature within $0.1^{\circ}C$.

The storage section, S, containing 1-butyne (or 1,2 butadiene) consisted of a series of two calibrated flasks separated by a mercury cut-off. This section was connected to

manometer M_1 . The total amount of gas which had flowed through during an experiment could be calculated from the difference of pressure recorded on M_1 . During storage the 1-butyne (1,2 butadiene) never came in contact with grease, being confined by a mercury cut-off, mercury manometer M_1 and a needle valve, NV. The gas was introduced into the stream of toluene via needle valve, NV, and through the tap T_2 and the internally sealed capillary G_2 . The backing pressure indicated on manometer M_2 was kept constant by adjustment of the needle valve. The total pressure in the reaction vessel, R, during a run was measured on the manometer M_3 to ± 0.001 cm. using a cathetometer.

The exit tube from the reaction vessel was heated with nichrome ribbon to prevent condensation of the products formed in the reaction. It contained a length of capillary tubing, C_3 , which controlled the rate of flow and led to a series of traps U, V and W. The first trap, U, was a U-tube of 10 mm O.D. fitted with two standard tapered ground glass joints. Traps V and W were of conventional design and were provided with standard tapered ground glass joints. A Leroy still (LS), a tilting McLeod gauge (TE), a gas burette (GB), and U-trap, k, was connected to the third trap via the tap T_6 shown in detail in Fig. 6 page 55.

A high efficiency Edwards - E mercury diffusion pump (DP) shown in Fig. 3 compressed the non-condensible

<u>Figure ó</u>

Analytical section of the apparatus



gases through a small trap, L, into the collection system (CS) which consisted of three calibrated bulbs connected in series by mercury cut-offs. A McLeod gauge, M, was connected to this section to measure the pressure of the non-condensible products. A Toepler pump, T, was also connected to this section. The Toepler pump led to a small gas burette which was joined to a small U-trap, J, and a small tube containing copper oxide, CF. Surrounding this small tube was an electrically heated furnace.

Gas Chromatography Apparatus

The apparatus for gas-liquid chromatography was essentially similar to that described by Callear and Ovetanovic (88). The power input was regulated with a Sorenson a.c. voltage regulator, model 5005. The d.c. low power regulator was kindly supplied by the Applied Chemistry Division of the National Research Council of Canada and was a homemade model providing a current at 6 volts with a noise less than one millivolt. A Gow-Mac thermal conductivity cell model TR11B with tungsten filaments was used as a detector. The resistance of this cell was adjusted with a 1.075 ohm Huirhead variable resistor type A-2-A. The off-balance signal was fed through an amplifier to a pen Speedomax Accorder Type G with full scale sensitivity of 50 millivolts. The amplifier used in this work was the c.c. Keithley micro-volt-ammeter model 150A with full scale sensitivities of ± 1 microvolt and ± 1

millimicroampere (with a power sensitivity greater than 4×10^{-19} watt.).

The apparatus was equipped with three separate columns all of $1/4^{"}$ inside diameter:

- (i) Separations of light hydrocarbons were made in a 50 ft. copper column filled with a mixture of tricresyl phosphate (T.C.P.) on fire brick (30% by weight T.C.P.). The column was operated at 90°C.
- (ii) For heavy hydrocarbons a 10 ft. glass
 column filled with 4% by weight dinonylph thalate on 270 mesh glass beads was used.
 This column was kept at room temperature.
- (iii) For aromatic compounds an 8 ft. glass column filled with Apiezon L grease on fire brick was employed. This column was heated to 60°C.

Procedure and Analysis

The system was evacuated to 10^{-5} mm pressure. After weighing, the toluene flask was attached through a standard tapered joint to the system. The toluene was frozen in liquid air and melted four times, and when frozen was degassed to 10^{-5} mm. To obtain the desired toluene pressure during an experiment the water bath was adjusted to the proper temperature. The pressure of the 1-butyne (or 1,2 butadiene) was recorded on manometer M_1 . Before commencing an experiment the three traps, U, V and N were surrounded with brine $(-5^{\circ}C)$, dry ice-acetone $(-78^{\circ}C)$ and liquid air $(-188^{\circ}C)$ respectively. Liquid air was also placed around the small trap, L, in the collection system to prevent the condensation of mercury from the hot diffusion pump on the walls of the collection system. Tap T₆ was closed. The mercury was raised in the Toepler pump to a designated level since the Toepler pump and combustion apparatus were not part of the calibrated collection system.

Toluene was then allowed to flow through the reaction vessel for 4 minutes with the collection system connected to the main vacuum line. This ensured the removal of any traces of permanent gas still dissolved in the toluene. Fumping into the main vacuum line was continued for a few minutes to completely remove from the collection system any small amounts of non-condensible gases generated by the pyrolysis of toluene itself. The collection system was then isolated from the main vacuum line by a mercury cut-off.

The needle value, NV, was opened. Then taps T_1 and T_2 were opened simultaneously allowing the toluene and 1-butyne (or 1,2 butadiene) to mix and flow through the hot reaction vessel. The 1-butyne (or 1,2 butadiene) was made to flow at a convenient rate which was determined by the backing pressure as indicated on manometer M_2 . The total pressure of the mixture of toluene and 1-butyne (or 1,2 butadiene) as indi-

cated on manometer \mathbb{N}_3 was usually kept at about 1.3 cm. The partial pressure of 1-butyne (or 1,2 butadiene) varied from about 1 to 570 of the total pressure. In order to change the pressure of the toluene in different experiments the temperature surrounding the toluene flask (F) was varied from 10 to 26° C. The time spent by the reacting mixture in the reaction vessel, i.e. the time of contact, could be varied from about 0.2 to 1.5 sec. by changing the capillary (C₃) in the outlet tube of the reaction vessel.

Usually the temperature and the pressure in the reaction vessel as well as the pressure in the collection system were recorded at 5 minute intervals throughout an experiment. For experiments shorter than 10 minutes these recordings were made at intervals of about 2 minutes. When a sufficient amount of non-condensible gas was collected, taps T_1 and T_2 were closed simultaneously stopping the flow of both toluene and 1-butyne (or 1,2 butadiene). To return the 1-butyne (or 1,2 butadiene), confined between tap T_2 and the needle valve (NV), to the storage section it was condensed by means of a cold "finger" surrounded by liquid air. The needle valve was then closed, the gas was allowed to expand, and the final pressure was recorded.

The pressure of the non-condensible gases was then measured by means of the McLeod gauge. In order to estimate the amount of non-condensible gases which were generated by the decomposition of toluene itself, tap T_1 was again opened and the toluene alone was allowed to flow for about 5 minutes. The increase in pressure was a measure of the amount of noncondensible gases formed from the decomposition of toluene alone. At the hignest temperatures used in these experiments (317° C) this amount was less than 10% of the total quantity of non-condensible gases produced by the decomposition of 1-butyne (or 1,2 butadiene) and it was negligible at the lowest temperatures (374° C). At the end of the experiment the toluene flask was removed and weighed.

Host of the dibenzyl, identified by its infra red spectrum, was recovered in the trap maintained at -5° C. The difference in weight of the trap before and after cleaning with toluene and ethyl ether represented the weight of dibenzyl. The dibenzyl had a slight yellow colour when the experiments were conducted in the highest temperature range of these experiments (790-817°C). A description of an attempt to identify this impurity will be given in a later section.

The trap at -80° J contained most of the toluene. The contents of the trap were removed for particular tests described in detail later.

The contents of the trap maintained at liquid air temperature were distilled through tap T_{C} into the small trap, n, which formed part of the gas burette (GB) shown in Fig. 6, page 55. The amount of material was estimated. The material

was then analyzed by vapour pressure measurements using a Leroy still (89). Individual components were separated and measured in the gas burette. These components were removed and their identity was confirmed by mass spectrometry or by infra-red spectroscopy. Most of the unreacted 1-butyne (or 1,2 butadiene) was found in this trap. In later experiments the components were separated by gas chromatography and identified by their infra-red spectra.

A portion of the non-condensible gases was removed from the collection system with the Toepler pump (T) and compressed into the combustion chamber filled with copper oxide (Fig. 3). Trap J was kept at -80°C. It was possible to compress the gaseous mixture from about 1-2 mm to about 300 mm in a few strokes of the Toepler pump. The initial pressure was recorded. The furnace surrounding the tube containing copper oxide was heated electrically to 300°C. and about 2 hours were allowed for complete combustion of the hydrogen to water, which was condensed in trap J. The furnace was allowed to cool to room temperature and the residual pressure, due to methane, was measured in the original volume. Thus, the composition of the non-condensible gases was determined. This technique was checked with known mixtures of methane and hydrogen and the accuracy was estimated at about 2-3%.
1-BUTYNE

Products and Results

The decomposition of 1-butyne was studied over the temperature range of $674-817^{\circ}$ C. The analysis of the noncondensible gases, shown in Table I, page 63, showed that in addition to methane various amounts of hydrogen were produced. The hydrogen content of these gases increased from $30_{7^{\circ}}$ to about $40_{7^{\circ}}$ with increase in temperature.

The amount of dibenzyl was always less than the amount of methane formed as shown in Table I, page ó3. As previously mentioned the dibenzyl was slightly yellow coloured in the temperature range 790-817°C. This was especially so when a low ratio of toluene to 1-butyne was used. Infra red spectra was taken of this dibenzyl using carbon tetrachloride as a solvent and compared to the spectrum of pure dibenzyl also using carbon tetrachloride as a solvent. The spectrum was not distorted in any way from that of pure dibenzyl. Hence the impurity could not be identified and it may be concluded that its presence must have been in very small amounts.

The unreacted toluene was trapped at -78°C. It always contained some unsaturated compounds dissolved in it, as shown by positive "spot tests" using a solution of potassium permanganate in acetone, and bromine dissolved in carbon tetrachloride. Blanks were done with the pure toluene with each reagent and gave negative results. This indicated that

<u>Table I</u>

Products from and rate constants for the Decomposition of 1-butyne

<u>Taole I</u>

Products of the Decomposition of 1-Butyne

Expt No	т°к	Total press cm	Partial press toluene cm	Partial press l-butyne cm	t sec	l-butyne [*] m.moles	Non- cond gases m.moles	%СН 4	% Dib/CH 4	k _l sec-l	k ₂ sec-1
82	948	1.61	1.56	0.05	1.40	1.270	0.111	68.7		0.05	0.02
16	949.5	1.22	1.17	0.05	0.30	4.380	0.072	73.9	-	0.03	0.02
83	949.5	1.84	1.81	0.03	1.23	Ú.831	0.073	63.8	-	Ú.05	0.03
22	954	1.39	1.35	0.04	Ŭ . 29	2.894	0.054	79.1	-	0.05	0.02
28	956	1.40	1.32	0.08	U.28	6.779	0.130	78.8	19.7	0.05	0.03
79	967	1.69	1.55	0.14	1.34	2.002	0.412	73.9	-	0.13	0.04
90 P	968.5	1.83	1.77	0.06	1.27	1.234	0.166	72.0	-	0.08	0.03
80	969	1.67	1.66	0.01	1.31	1.115	0. 219	62.5	-	0.10	0.02
81	969	1.68	1.59	0.09	1.31	1.414	0.264	73.0	-	0.12	Ú.04
21	969	1.34	1.33	0.01	0.28	0.815	0.293	80.6	-	0.12	0.04
6	975.5	1.34	1.33	0.01	0.30	2.110	0.083	87.1	31.2	0.12	0.02
84	976.5	2.02	2.00	U.U2	1.09	0.970	0.179	63.5		0.11	0.07

x Total amount of 1-butyne flowed through during time of experiment.

Table [I (Co	ntin	ued)

Expt No	$T^{\mathbf{O}_{K}}$	Total press cm	Partial press toluene cm	Partial press l-butyne cm	t sec	l-butyne [#] m.moles	Non- cond gases m.moles	% ^{Ch} 4	% Dib/CH ₄	kl sec-l	k ₂ sec-l
24	977	1.27	1.25	0.02	0.28	1.451	0.069	77.1	9.4	0.13	0.04
23	977•5	1.32	1.29	0.03	0.29	2.481	0.11 7	77.8	11.4	0.13	0.04
19	980.5	1.47	1.44	0.03	U.29	2.470	0.136	83.3	22.1	0.16	0.04
17	983	1.16	1.10	0.06	0.20	5.450	0.265	77.0	39.2	0.20	0.06
89P	986	1.83	1.69	0.14	1.20	0.932	0.255	70.6	_	0.19	0.08
78	994	1.63	1.58	0.05	Ú.53	2.058	0.281	71.4	-	Ü.20	6.08
26	995	1.35	1.33	0.02	0.28	1.271	0.098	71.2	34.8	0.20	80.0
27	999	1.41	1.39	0.02	0.28	1.385	0.105	80.2	~	0.23	0.05
68	999.5	1.49	1.43	U.06	0.51	2.461	0.455	66.6	-	0.27	U.14
25	1001	1.40	1.38	0.02	0.28	2.240	0.201	75.6	27.6	0.28	0.07
64	1002	1.34	1.28	0.06	0.28	4.125	U.38 9	73.8	-	Ū.25	0.08
67	1002	1.47	1.43	0.03	0.52	2.285	0.405	67.1	-	0.25	0.13
66	1002.5	1.32	1.24	0.08	0.29	4.061	0.402	74.1	-	0.28	0.09
65	1003.	1.21	1.16	0.05	0.30	2.690	U.259	71.4	-	0.24	0.10

Table I (Continued)

Expt No	T ^o k	Total press cm	Partial press toluene cm	Partial press 1-butyne cm	t sec	l-butyne [¥] m.moles	Non- cond gases m.moles	シ₀CH ₄) Dib/CH ₄	k _l sec-l	k ₂ sec-1
5	1003	1.34	1.29	Ú.05	0.27	6.490	0.552	78.1	32.5	0.26	0.06
4	1008.5	1.37	1.33	Ü.04	0.26	5.640	0.630	79.9	43.7	U.3 6	0.10
85	1008.5	1.96	1.91	0.05	1.13	0.338	0.202	58.1	-	0.47	Ü.34
41	1011.5	1.32	1.30	Ū.Ú2	0.21	2.196	0.242	76.4	30.3	U.42	0.13
42	1013.5	1.33	1.27	0.06	0.27	2.062	0.265	74 . 0	19.5	0.34	0.16
88P	1014	1.96	1.89	0.07	1.16	0.484	0.226	60.0	-	0.32	0.22
62	1017	1.28	1.21	0.07	0.30	2.501	0.652	64 . Ŭ	28.6	0.54	0.48
43	1017.5	1.34	1.31	0.03	0.27	3.510	0.520	76.4	19.0	Ū.46	Ũ . 14
77	1018	1.59	1.56	0.03	0.53	1.119	Ũ . 338	69.7	38 . 0	0.47	0.16
76	1018.5	1.82	1.79	0.03	0.47	1.158	0.375	72.6	41.0	0.60	0.22
40	1020.5	1.32	1.30	0.02	0.29	0.966	0.154	80.5	-	0.51	0.44
69	1022.5	1.46	1.43	0.03	0.51	U.837	0.308	59.7	-	0.54	0.37
34	1025	1.49	1.46	0.03	0.29	1.155	0.250	70.2	38.2	ü.60	0.25
63	1027	1.11	1.01	0.10	0.30	1.829	0.455	67.7	-	0.62	0.34

	Table I (Continued)										
Expt No	т ^о к	Total press cm	Partial press toluene cm	Partial press l-butyne cm	t sec	l-butyne ^x m.moles	Non- cond gases m.moles	‰CH ₄	% Dib/CH 4	kl sec-l	k ₂ sec-1
86	1030	2.00	1.95	0.05	1.06	U.250	0.206	55.0	-	0.90	0.74
33	1031	1.58	1.57	0.01	Ú.26	0.622	0.131	79.7	41.5	0.73	0.19
91P	1031	1.95	1 <u>.</u> 84	0.11	1.11	0.631	Û.455	57.4	42.4	U.66	0.49
32	1033.5	1.44	1.43	0.01	0.27	0.118	0.033	79.2	-	0.96	0.25
2	1034	1.42	1.33	0.09	0.21	2.160	0.394	75.9	-	0.76	0.20
3	1035	1.57	1.17	0.40	Ú.22	2.730	0.551	78.7	-	0.90	0.12
75	1035	1.73	1.70	0.03	0.49	1.203	0.585	66.4	57.0	0.90	U.46
71	1035.5	1.58	1.52	0.06	0.48	0.994	0.460	59.8	35.6	0.79	0.49
70	1036	1.58	1.54	0.0 4	0.49	0.632	0.278	58.2	24.8	0.69	0.50
29	1039	1.35	1.33	Ü,Ü2	U.26	1.435	Ü.351	08.7	43.1	0.80	0.37
56	1039	0.81	U.78	0.03	0.29	1 . 369	0.431	69.6	64.5	0.91	0.40
48	1042.5	1.25	1.23	0.02	U.29	0.701	0.186	69.0	42.4	0.79	0.29
11	1044	1.34	1.29	0.05	0.26	2 . 990	0.832	69.3	23.2	6. 86	0.39
49	1044	1.21	1.15	0.0 6	0.27	1.292	U.378	65.8	29.9	0.85	0.44

	Table I (Continued)										
Expt No	T ^o k	Total press cm	Partial press toluene cm	Partial press l-butyne cm	t sec	l-butyne [*] m.moles	Non- cond gases m.moles	7₀СН 4	% Dib/CH 4	k _l sec-l	k ₂ sec-l
47	1045	1.10	1.07	0.03	0.32	1.364	0.391	67.8	30.4	0.74	0.30
35	1046.5	1.41	1.38	0.03	0.28	0.863	0.378	62.6	44•4	1.20	0.27
55	1050	1.57	1.56	0.01	0.26	0.524	0.248	69.2	62.4	1.68	0.69
61	1050	1.26	1.23	0.03	0.27	0.691	0.316	62.2	51.8	1.44	0.87
57	1053	1.44	1.42	0.02	0.27	0.819	0.437	62.5	64.5	1.77	1.04
8	1053.5	1.35	1.30	0.05	0.25	2.670	0.865	67.3	34.9	1.07	0.49
60	1055	1.31	1.20	0.11	0.24	1.277	0.632	59.8	-	1.74	1.17
54	1056	1.17	1.10	0.07	0.26	1.768	0.666	77.0	-	1.38	0.41
36	1056.5	1.24	1.21	0.03	0.27	0.934	0.450	61.1	51.7	1.53	1.12
53	1057	1.02	0.97	0.05	0.27	1.142	0.433	77.3	20.3	1.36	Ú.4Ú
39	1058	1.37	1.34	0.03	0.27	0.893	U.468	60.3	50.7	1.66	1.10
9	1060	1.14	1.11	0.03	0.29	1.740	0.081	69.3	31.5	1.17	0.53
58	1060.5	U. 98	0.96	0.02	0.31	0.797	0.506	04.1	38.1	2.09	1.16
74	1063	1.63	1.60	0.03	0.48	0.475	0.410	61.5	50.1	2.52	1.59

		Table I (Continued)									
Expt No	T ^o k	Total press cm	Partial press toluene cm	Partial press l-butyne cm	t sec	l-butyne ^x m.moles	Non- cond gases m.moles	^{удСП} 4	[%] Dib/CH ₄	kl sec-l	k ₂ sec-1
13	1064.5	1.39	1.33	0.06	0.28	3.120	1.380	66.0	51.9	1.38	0.72
37	1066.5	1.30	1.27	0.03	0.23	0.915	0.514	59.9	-	2.16	1.45
59	1068	0.85	0.81	0.04	0.16	1.278	0.636	57.0	38.7	2.58	1.70
15	1069	1.39	1.37	0.02	0.20	1.220	0.612	70.6	54.8	2.43	1.02
7	1071	1.43	1.42	0.01	0.22	1.050	0.814	70.3	-	2.68	1.14
14	1072	1.37	1.31	0.07	0.29	1.390	0.699	90.4	23.6	2.18	0.23
12	1074	1.25	1.24	0.01	0.18	0.800	0.323	70.5	60.5	3.21	1.28
38	1074.5	1.33	1.30	0.03	0.26	0.735	0.524	67 . Ü	44.9	2.98	1.78
44	1090	1.16	1.14	0.02	0.20	0.598	0.514	61.3	-	5.32	4.10

some of the unreacted 1-butyne and probably some of the products were dissolved in the toluene. To determine the extent of solubility of 1-butyne in toluene several experiments were done under identical conditions used for the pyrolysis except that the furnace was at room temperature. Only about 60% of the 1-butyne was recovered in the trap immersed in liquid air, the rest remaining dissolved in the toluene. In later experiments a drop of toluene, recovered from trap V, was passed through the T.C.F. gas chromatographic column and was shown to contain part of the unsaturated products of pyrolysis (allene, propyne and vinyl acetylene) in addition to the unreacted 1-butyne dissolved in it. Even repeated distillation of the toluene recovered from trap V did not lead to quantitative removal of the 1-butyne and the unsaturated products from the toluene, which was in a 100-1000 fold excess. Hence it was difficult to establish a mass balance in terms of all the reaction products.

The liquid air trap contained most of the unreacted 1-butyne together with some of the products of pyrolysis. These compounds were separated from the 1-butyne by means of the Leroy still. By vapour-pressure analysis the products were found to be ethane, propyne, and a C₆-fraction. The identity of the ethane and propyne was confirmed by mass spectrometry. The amount of ethane was extremely small and never more than 1% of the methane formed and was, therefore, neglected in the calculations of rate constants. The C₆- fraction was found to have a mass of 76 by mass spectrometry. In later experiments this fraction was also passed through the Apiezon L grease column of the gas chromatography apparatus. Two compounds, of different elution time, were separated from each other and were identified again by means of the mass spectrometer. Both compounds had a mass of 78. Since the formation benzene was expected (from the decomposition of toluene itself according to the scheme shown on page 41) it was concluded that a compound of mass 78 (other than benzene) was formed in the reaction. By mass spectrometry the C_4 fraction was snown to contain a compound of mass 52 in addition to 1-butyne but it could not be separated from the latter using the Leroy still.

In the latter stages of this work, when the apparatus for gas chromatography was built, the contents of the liquid air trap were transferred into the gas chromatography apparatus. A typical separation for the light hydrocarbons is shown in Fig. 7, page 66. As can be seen, the presence of ethane, allene, propyne, 1-butyne and vinyl acetylene^X was demonstrated. The allene was separated out and its identity was confirmed by infra-red spectroscopy. The ratio of propyne to allene was 3/2 under various conditions of experimentation. This estimate was made from a comparison of their peak areas, with no correction made for a possible

^{*} Vinyl acetylene corresponds to the compound of mass 52 previously referred to.

Figure 7

Separation of light hydrocarbons on T.C.P. Column of the gas chromatography apparatus



difference in their sensitivities. The total quantity of the C_3 compounds (allene and propyne) was estimated to amount to about 1/6 of the methane formed at the hignest temperatures employed in these experiments. A similar estimate was obtained using the Leroy still in combination with the gas burette. At the lower temperatures the amount of the C_3 compounds formed appeared to be less than 1/6 of the methane formed; however no definite estimate of the amount of C_3 compounds formed at the lower temperatures could be made in view of the small peaks given by these compounds. The compound of mass 52 was separated out and its infra-red spectrum was demonstrated to be identical with that of vinyl acetylene. The vinyl acetylene^X was obtained from Dupont Co., Louisville, hentucky, as a 50% solution by weight in xylene to which had

¥	Vinyl acetylene	is a	very	dangerou	us mate	rial	to	handle	and
	the following ha	azards	are	quoted f	from th	e spe	ecii	fication	l
	sheet obtained :	from D	upont	; Co.					

- Under certain conditions it will form explosive acetylides in the presence of copper or copper-bearing alloys, silver, or mercury, or the salts of these metals.
- (2) It forms explosive mixtures with air over a wide range of conditions, resembling acetylene in this respect.
- (3) It can be exploded in the absence of air if strongly enough incited, especially under pressure.
- (4) Temperatures above 100° C must be avoided because it may be extremely unstable under these conditions.
- (5) It will form peroxides in the presence of air and they are violently explosive.
- (6) It gradually polymerizes during storage and the polymers will also peroxidize.
- (7) It will polymerize with violence if it is exposed to polymerizing catalysts (e.g. polyvalent halides).

been added P-tertiarybutylcatechol. The vinyl acetylene was technical grade and contained from 4% to 6% by weight of acetaldehyde and from 170 to 270 chlor bodies. It was purified by repeated distillation at low pressure in a chemically clean apparatus containing no mercury, and subsequently passed through the T.C.P. column of the gas chromatography apparatus for further purification. It had the same elution time as the C_{i} compound in guestion and showed an identical infra-red spectrum. The amount of vinyl acetylene accounted for was usually larger than 70% of the hydrogen produced. This represents only a lower limit of the amount of vinyl acetylene formed in the reaction since some of this compound could not be readily separated from the toluene. As will be shown later on the basis of the proposed mechanism for the pyrolysis of 1-butyne it is reasonable to suggest that in actual fact the amount of vinyl acetylene formed was equal to the amount of hydrogen formed.

DISCUSSION

Mechanism of Decomposition

From these results it is suggested that the thermal decomposition of 1-butyne could be accounted for by two simultaneous, rate-determining, unimolecular processes,

$$CH = C - CH_2 - CH_3 \xrightarrow{\kappa_1} CH = C - CH_2 \cdot + CH_3 \cdot (1)$$

$$CH \equiv C - CH_2 - CH_3 \xrightarrow{\kappa_2} CH \equiv C - CH = CH_2 + H_2$$
(2)

reaction (1) being predominant and that each CH_3 radical produced in reaction (1) yielded subsequently one molecule of methane by abstracting a hydrogen atom from toluene.

$$CH_3 \cdot + C_6H_5CH_3 \longrightarrow CH_4 + C_6H_5CH_2 \cdot$$
 (3)
The rate of formation of metnane was considered to be a
measure of reaction (1). Similarly if it is assumed that
hydrogen is formed exclusively by reaction (2), then the
production of hydrogen is a measure of reaction (2). The
rate of disappearance of 1-butyne, A, may then be written
as

$$-\frac{dA}{dt} = (k_1 + k_2)A = kA$$

where k is the overall rate constant for the disappearance of 1-butyne. Then,

$$A = A_0 e^{-kt}$$

where A_0 is the initial concentration of 1-butyne, and the rate of formation of methane is given by

or
$$\frac{d(CH_4)}{dt} = k_1 A = k_1 (A_0 e^{-kt})$$
$$\int_0^t (CH_4) = \frac{k_1}{k} A_0 (1 - e^{-kt})$$

The overall rate constant, k, was calculated from the rate of formation of $(H_2 + CH_4)$,

i.e.
$$k = \frac{2.303}{t} \log \frac{A_0}{(A_0 - (H_2 + CH_4))}$$

and the rate constant k_1 could then be calculated from the measured yields of methane. The rate constant, k_2 , represents the difference between the two rate constants, k-k₁. A list of the calculated values for k_1 and k_2 are shown in Table I, page 63. The rate constant k_1 at a given temperature was not affected, within experimental accuracy, by the variation of the reaction time by a factor of four, of the partial pressure of 1-butyne by a factor of three, and of the toluene pressure by a factor of up to two. These results are shown in Tables II, III and IV on pages 71, 72 and 73, respectively. It is also evident from Table V, page 74 that the increase in surface to volume ratio by a factor of 14 did practically not affect the rate constant k_1 .

Calculation of Activation Energies

The plot of log k_1 vs. 1/T, shown in Fig. 8, page 75, was linear over the temperature range studied. From the slope of this line the activation energy of reaction (1) was calculated as 67 kcal/mole and the frequency factor in the Arrhenius equation as $1.4 \times 10^{14} \text{sec}^{-1}$.

The largest source of error in the experimental measurements was considered to be the uncertainty in determining the exact temperature of the reaction vessel during an experiment. This uncertainty was due to fluctuations of the temperature in the reaction vessel in spite of the large heat capacity of the furnace and to the variation of the temperature along the length of the reaction vessel. The estimated

Table II

Expt No	T^{o_k}	Time of Contact sec	k _l sec-l
16	949•5	0.30	0.05
83	949.5	1.23	0.05
21	969	0.28	0.12
81	969	1.31	0.12
24	977	0.28	0.13
84	976.5	1.09	0.11
26	995	Ŭ.28	0.20
78	994	0.53	0.20
27	999	0.28	0.23
68	999.5	0.51	0.27
64	1002	0.28	0.25
67	1002	0.52	0.25
43	1017.5	Ü.27	0.46
77	1018	0.53	0.47
40	1020.5	0.29	0.51
69	1022.5	0.51	Ü.54
3	1035	0.22	0.90
75	1035	0.49	0.90

Effect	of	Reaction	n Time	on	First-Order
		Rate Cor	nstant	, k _]	L

Table III

on	First-Urder	mate Constant,	ĸı
Expt No	т ^о к	l-Butyne Press cm	kl sec-l
б	975.5	0.01	0.12
24	977	0.02	0.13
5	1003	0.05	0.26
66	1002.5	Ú.UŠ	0.28
34	1025	0.03	0.60
63	1027	0.10	Û.62
75	1035	0.03	0.90
3	1035	0.40	0.90
48	1042.5	0.02	0.80
49	1044	0.06	0.85
36	1056.5	0.03	1.53
54	1056	0.07	1.38
12	1074	0.01	3.21
38	1074.5	0.03	2.98

Effect of Partial Pressure of 1-Butyne on First-Order Rate Constant, k₁

Table IV

Expt No	T ^o k	Toluene Press cm	kl sec-l
83	949.5	1.84	0.05
16	949•5	1.17	0.03
84	976.5	2.02	0.11
24	977	1.25	0.13
76	1018.5	1.79	0.60
40	1020.5	1.30	Ũ . 51
75	1035	l.70	0.90
56	1039	0.78	Ŭ.91
39	1058	1.34	1.66
53	1057	0.98	1.36
74	1063	1.60	2.52
58	1060.5	0.96	2.09
37	1066.5	1.27	2.16
59	1068	0.81	2.58

Effect of Toluene Pressure on First-Order Rate Constant, k₁

Table v	\mathbf{T}_{i}	ab	le	V
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Effect of Packed Reaction Vessel on First-Order Rate Constant, k₁

		k,
Expt No	$T^{O_{K}}$	sec-l
80	969	0.10
90P	968.5	60.08
17	983	0.20
89P	986	Ú.19
42	1013.5	0.34
88P	1014	0.32
33	1031	Ú.73
91P	1031	0.66

Figure 8

Plot of log k_1 vs. 1/T

Filled circles denote experiments done in packed reaction vessel



fluctuation in the temperature was not more than $+2^{\circ}K$. Although this represents a small percentage error in the temperature range used, the resulting percentage error in the rate constant is large. For example, from the plot of log k_1 vs. 1/T given in Fig. 8, page 75, the corresponding rate constants at the temperatures 1023° h and 1025° k (which are approximately in the middle of the temperature range used in these experiments) are 0.54 and 0.57 \sec^{-1} respectively. The error in the rate constant resulting from an uncertainty of 2°k is thus about 6,. However, from the graph the greatest deviation would correspond to a temperature uncertainty of 7° and therefore one must conclude that additional sources of error might have been involved. For most experiments the deviations from the line could be accounted for to a large extent by the fluctuation of temperature.

In order to improve the accuracy of the computed activation energy one could either extend the temperature range or increase the accuracy of the estimated rate constants. The extension of the temperature range is limited, however, by technical problems. As in the present study the reaction at higher or lower temperatures may be unsuitable for experimentation being too rapid or too slow. Alternately, the values of the rate constants can be made more reliable by

x An error of about c_{10} in the rate constant, κ_1 , would result in an error of not more than 1 kcal/mole in the activation energy for reaction (1).

frequent repetition of individual runs. Repetition of individual runs leads to improvement of the results only when the experimental errors are of the random type.

Another source of error may result as a consequence of assigning an activation energy to a specific reaction, since there may be some uncertainties inherent in the assumption of a reaction mechanism. Side reactions may affect the products by which the rate of the primary step is measured. The magnitude of such errors are difficult to assess, particularly when some of the possible side reactions may not nave been accounted for. The plot shown in Fig. 8, page 75 represents all the results obtained in this study under a variety of experimental conditions including variation of the time of contact, of total pressure and partial pressure of the reactants, and of the surface to volume ratio. Obviously some of the side reactions may become more pronounced under certain conditions and the effect of "lumping" all the results together may explain some of the scatter.

Obviously amongst the additional sources of error contributing to the scatter of the rate constants one could include the inaccuracy of the determination of the composition of the non-condensible gases, and errors involved in the calculation of the time of contact. The latter source of error is primarily due to small fluctuations in the total pressure in the reaction vessel during an experiment. No attempt was made to assess the magnitude of these additional errors, since it was difficult to estimate their contributions.

In spite of these errors which are reflected in the scatter of the values for the rate constants the activation energy of 67 kcal/mole was considered to be accurate within ± 2 kcal/mole. This estimate is based on the fact that the extreme values for the activation energy calculated from the points in Fig. 8, page 75 were 69.0 and 65.0 kcal/mole.

The plot of log k_2 vs. 1/T is given in Fig. 9, page 79 and the "best" line was drawn somewhat arbitrarily in view of the rather large scatter of the experimental results. An examination of this graph shows that the reaction was not affected within experimental accuracy by increasing the surface/volume ratio. From the slope of the line the activation energy of reaction (2) was calculated as 78+ (?) kcal/mole and the frequency factor in corresponding Arrnenius equation as 10^{16} sec⁻¹. The plot of log k₂ vs. 1/T shows much more scatter than the corresponding plot for reaction (1). This is to be expected since rate constant \boldsymbol{k}_2 represents the small difference between two larger rate constants \boldsymbol{k} and \boldsymbol{k}_{l} . The errors involved in the calculation of $k_{\mathcal{D}}$ are magnified as compared to the errors involved in the calculation of ${\bf k}_1$. Hence no attempt was made to evaluate the error for the activation energy of reaction (2) since it was felt that the calculated value of 78 kcal/mole can be considered at best a rough estimate for the activation energy of reaction (2).

Figure 9

Plot of log k_2 vs. 1/T

Filled circles denote experiments done in packed reaction vessel



Fate of the Propargyl Radical

As stated in the introductory section the C_3H_3 radical may be considered to resonate between at least the two canonical structures, i.e. one corresponding to that of the propargyl radical and the other corresponding to that of the allenyl radical:

$$CH \equiv C - CH_2 \cdot \longleftrightarrow CH_2 = C = CH \cdot \tag{4}$$

In fact the formation of propyne and allene in the present study may be taken as evidence that this radical in its reactions with toluene was able to react both as a propargyl radical and as an allenyl radical:

$$CH \equiv C - CH_2 \cdot + C_0 H_5 CH_3 \longrightarrow CH \equiv C - CH_3 + C_0 H_5 CH_2 \cdot (5)$$

$$CH_2 = C = CH \cdot + C_6H_5CH_3 \longrightarrow CH_2 = C = CH_2 + C_6H_5CH_2 \cdot (6)$$

The ratio of propyne to allene formed was found to be 3:2 under varying conditions of temperature. If both ends of the C_3H_3 radical were equally reactive with toluene, one would expect to find equal amounts of propyne and allene formed. It is difficult to visualize why one end of the radical should be more reactive. In principle, another possibility to be considered is that the activated complex resulting from the collision of a C_3H_3 radical with a toluene molecule can rearrange to form the more stable product. The heats of formation of propyne and allene are 44.32 and 45.92 kcal/mole respectively (82). Therefore to all intents and purposes the stability of the two products, propyne and allene, may be considered identical, and one must conclude that propyne is found in excess of allene because the $^{C}3^{H}3$ radical approximates more closely the propargyl configuration.

The sum of the C_3 products, (allene and propyne), was estimated to be 1/6 of the methane formed at the highest temperature used in this investigation ($817^{\circ}C$). These C_3 products are a result of a normal mode of reaction of free radicals with toluene, i.e. the abstraction of a hydrogen atom. But apparently a large proportion of C_3H_3 radicals were removed by reactions other than (5) and (6), i.e. by reactions involving their dimerization or combination with benzyl radicals:

$$2 \circ_{3} H_{3} \cdot \longrightarrow \circ_{6} H_{6} \tag{7}$$

$$c_{3}\Pi_{3}^{\bullet} + c_{6}\Pi_{5}C\Pi_{2}^{\bullet} \longrightarrow c_{6}\Pi_{5}C\Pi_{2}C_{3}\Pi_{3}$$
(8)

Indeed this was confirmed experimentally. A compound of mass 78 (other than benzene) was found by mass spectrometry. However, attempts to isolate it from the large excess of toluene were not too successful and hence sufficiently large samples could not be obtained to determine its exact structure using infra-red spectroscopy. The compound from several experiments were accumulated but could not be characterized since it seemed to disappear with time. This may have been due to its absorption in the grease or to its polymerization.

Collin and Lossing (83) showed by mass spectrometry that the $C_3^{H}_3$ radicals, produced in the mercury photosensitized decomposition of allene, dimerized to give a $C_6^{H}_6$

compound. Farmer and Lossing (87) also found a $C_6^{H_6}$ compound by mass spectrometry in their study of the thermal decomposition of propargyl iodide. Although identification of this ${\rm C}_{6}$ compound was not made, they assumed that this compound resulted from the dimerization of the generated propargyl radicals and had the dipropargyl structure. More recently, Srinivasan (84) suggested that the C_3H_3 radical derived from the photodecomposition of 1,3 butadiene dimerized to give two different products of mass 78, which he was able to separate by gas chromatographic methods. The weight of all this evidence demonstrates that the C_3H_3 radical is reluctant to abstract hydrogen atoms and that it dimerizes. Since in the present system there are at least as many benzyl radicals as C_3H_3 radicals, it is not unlikely that these two radicals may combine to give a C_{10} product according to reaction (8). A product of this type would be expected to condense in the trap maintained at -80°C, along with the unreacted toluene. No attempt was made to isolate the C_{10} compound(s) since the toluene was obviously in a large excess. Nevertheless it ought to be mentioned that a trace amount of a C_{10} compound was detected by mass spectrometry in a fraction isolated by the Leroy still, which contained primarily C_6 compounds and toluene. This compound may actually be the $C_{10}H_{10}$ compound expected according to reaction (8).

Formation of Dibenzyl

Dibenzyl is formed from the dimerization of the

benzyl radicals produced in reactions (3), (5) and (6):

$$2 \ c_{6}^{H} _{5}^{CH} _{2} \longrightarrow (c_{6}^{H} _{5}^{CH} _{2})_{2} \tag{9}$$

Stoichiometrically the amount of dibenzyl formed would be expected to be equal to the amount of methane formed in the reaction if all the $\text{CH}_3^{\texttt{X}}$ and C_3H_3 radicals abstracted hydrogen atoms from the toluene, and if all the benzyl radicals dimerized to give dibenzyl. From an inspection of Table I it can be seen that the amount of dibenzyl was much smaller than that of methane. This supports the supposition that a considerable amount of C_3H_3 radicals is removed by their dimerization (reaction 7) and by their combination with benzyl radicals (reaction 8).

Thermal Stability of the C3H3 Radical

If the $C_{3}H_{3}$ radical decomposes in the hot reaction vessel, then one might expect to find ethylene or acetylene amongst the products, and also the reaction vessel might be coated with carbon. Acetylene and ethylene were not formed. Also an examination of the reaction vessel and of the tubing leading from it did not snow any presence of carbon. Hence it can be concluded that the $C_{3}H_{3}$ radicals do not further decompose under the experimental conditions used.

Abstraction of hydrogen atoms from toluene by methyl radicals will be treated in the discussion of the decomposition of 1,2 butadiene.

Hydrogen Producing Step

It was suggested earlier that the hydrogen produced could be accounted for by reaction (2) involving the molecular mechanism:

$$CH \equiv C - CH_2 - CH_3 \longrightarrow CH \equiv C - Ch = CH_2 + H_2$$
(2)

nowever the production of hydrogen could be also explained by an alternate, free radical mechanism:

$$CH \equiv C - CH_2 - CH_3 \longrightarrow CH \equiv C - CH - CH_3 + H \cdot$$

$$CH \equiv C - \dot{C}H - CH_3 \longrightarrow CH \equiv C - CH = CH_2 + H \cdot$$

$$(10)$$

$$(11)$$

Generally, the temperature needed to rupture a normal C-H bond is much higher than those used in this study. It can be argued, however, that the C_4H_5 radical, which might be produced by the rupture of the secondary C-H bond in 1-butyne, would be stabilized by resonance due to its ability to exist in at least the two canonical structures similar to those of the C_3H_3 radical, i.e.

$$CH = C - \dot{C}H - CH \not\longleftrightarrow \rightarrow CH = C = CH - CH_{3}$$
(12)

and that in consequence the corresponding C-H bond dissociation energy is lowered appreciably with respect to $D(CH_3-H)$. The C_4H_5 radical could then lead to a stable product by one of the following reactions:

> (1) it could abstract a hydrogen atom from toluene to reform one molecule of 1-butyne, or to generate a molecule of 1,2 butadiene.
> CH=C-CH-CH₃ + C₆H₅CH₃→ CH=C-CH₂-CH₃ + C₆H₅CH₂. (13) CH₃-CH=C=CH. + C₆H₅CH₃→CH=C=CH-CH₃ + C₆H₅CH₂. (14)

- (2) it could dimerize or combine with another free radical participating in the reaction system.
- (3) it could further decompose by splitting off one H atom and thus generate a molecule of vinyl acetylene (reaction ll).

Case (1) can be ruled out since 1,2 butadiene was not detected amongst the products of the reaction. Case (2) can be ruled out on similar grounds, since the corresponding dimer $C_{8}^{H}_{10}$ was not detected in the fractions isolated by gas chromatography. Similarly, neither a C_{11} nor C_{7} compound, which could have been derived from the combination of the $C_{4}^{H}_{5}$ radical with either a benzyl radical or a $C_{3}^{H}_{3}$ radical, was detected.

however case (3) cannot be easily disposed of since it could, in principle, account for both the formation of H_2 and vinyl acetylene:

$$CH \equiv C - CH - CH_3 \longrightarrow CH \equiv C - CH = CH_2 + H$$
 (11)

The hydrogen atoms generated in steps (10) and (11) would be expected to be removed by reactions with the excess of toluene, according to the following scheme:

$$H \bullet + C_6 H_5 C H_3 \longrightarrow H_2 + C_6 H_5 C H_2 \bullet$$
(15)

$$H^{\bullet} + C_{6} H_{5} C_{6} H_{6} + C H_{3} \bullet$$
 (16)

$$H \bullet + c_{6}H_{5}CH_{3} \longrightarrow c_{6}H_{5} \bullet + CH_{4}$$
(17)

Furthermore, for each mole of hydrogen produced by reaction (15), a mole of benzyl radicals would be formed and therefore if reactions (10) and (11) occurred one would have expected that the dibenzyl produced would have been larger than the

amount due to reaction (1) provided that some of the benzyl radicals had not been removed by combination with C_3H_3 radicals. From an inspection of Table I, page 53 it can be seen that usually the dibenzyl amounted to only 30-40% of the methane formed. Hence this evidence does not support reactions (10) and (11). A more definite conclusion cannot be made on the basis of the results obtained in this study since the low yields of dibenzyl have previously been explained as being due to the combination of a benzyl radical with a C_3H_3 radical. However, some indirect, but sufficiently plausible arguments against the participation of reactions (10) and (11) can be offered:

The values for the rate constant, k_1^{l} , were calculated on the assumption that reactions (10) and (11) did actually occur.^{*} According to reactions (16) and (17) some H atoms would disappear and generate instead methane. Szwarc (47) stated that the ratio of hydrogen to methane formed as a result of reactions (15), (16) and (17) was 3/2 and independent of temperature. Therefore the amount of methane formed by these reactions is equal to 2/3 of the amount of hydrogen produced. Taking into consideration that for every mole of 1-butyne disappearing via reactions

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x k₁ represents the rate constant of reaction (1) calculated on the assumption that reactions (10) and (11) are exclusively responsible for the production of nydrogen.

(10) and (11) two moles of $(H_2 + CH_4)$ would be formed, the following relationships can be deduced for the overall rate constant for the disappearance of 1-butyne and for the rate constant of reaction (1):^{**X**}

$$k_{o} = \frac{2.303}{t} \log \frac{A_{o}}{(A_{o}) - ((CH_{4}) + 1/6(H_{2}))}$$
$$k_{1}^{1} = \frac{k_{o}((CH_{4}) - 2/3(H_{2}))}{A_{o}(1 - e^{-kot})}$$

The rate constant for reaction (1) was calculated by this method for several temperatures and the logarithms of these values were plotted against 1/T as shown in Fig. 10, page 88. The activation energy, determined from the slope of the line drawn in Fig. 10, page 88 was 62.5 kcal/mole with the usual assumption that the recombination of the radicals produced in reaction (1) requires no activation energy, the activation energy of 62.5 kcal/mole could be identified with $D(CH;C\cdot CH_2-CH_3)$. This value is essentially identical with the corresponding C-C bond dissociation energy in 1-butene

For a unimolecular decomposition
$$k = \frac{2.303}{t} \log \frac{A_0}{A_0 - x}$$

where x is equal to the number of moles decomposed in
time t.
The number of moles of 1-butyne decomposed due to reaction
(1) = total CH_4-CH_4 generated by reactions (16) and (17)
= $CH_4 - 2/3 H_2$.
The number of moles of 1-butyne decomposed according to
reactions (10) and (11) = $1/2(H_2 + CH_4)$ formed due to
reactions (16) and (17) = $1/2(H_2 + 2/3 H_2)$
Total number of moles of 1-butyne decomposed = x =
 $(CH_4) + 1/6(H_2)$.

<u>Figure 10</u> Flot of log k_l¹ vs. 1/T


for which Sehon and Szwarc (81) proposed the value of 01.5 kcal/mole. If the C-C bond dissociation energy in 1-butyne was indeed identical to the corresponding bond dissociation energy in 1-butene, the resonance energy of the $\rm C_3H_3$ radical would be equal to that of the allyl radical, $CH_2 = CH_2 CH_2 \cdot$. However it seems reasonable that the resonance stabilization of the C_3H_3 radical should be considerably less than that of the allyl radical, since the latter radical ought to be maximally stabilized due to its ability to resonate between two identical canonical structures. This reasoning is also supported by the fact that the dissociation energies for the propargyl halides are 8-10 kcal/mole greater than those of the corresponding allyl halides (87, 70). Therefore it seems very likely that the C-C bond dissociation energy in 1-butyne is greater than the corresponding bond in 1-butene and that hence the production of hydrogen cannot be explained satisfactorily by reactions (10) and (11).

Moreover even if one assumed that the resonance energy of the C_4H_5 radical were equal to that of the C_3H_3 radical, on general grounds, the C-H bond dissociation energy, $D(CH_3^*C \cdot CH \cdot CH_3)$ would be expected to be stronger than H

the corresponding C-C bond dissociation energy, D(CH:C·CH₂-CH₃), by some 15 to 18 kcal/mole, and therefore, under propitious conditions for reaction (1) reaction (10) and consequently reaction (11) would be negligible. This argument would be valid only provided the frequency factor in the Arrhenius equation for reaction (10) had a "normal" value of 10¹²-10¹⁴sec⁻¹.

In conclusion, it is felt that on the basis of all these arguments, reactions (10) and (11) can be excluded from the mechanism of decomposition and that the production of hydrogen can be accounted for by the molecular mechanism represented by reaction (2), and that the method of calculating k_1 was justified.

Conclusions

In summary, the complete mechanism for the thermal decomposition of 1-butyne in an excess of toluene can be represented by the following scheme:

$$CH = C - CH_2 - CH_3 \xrightarrow{k_1} CH = C - CH_2 \cdot + CH_3 \cdot$$
 (1)

$$CH = C - CH_2 - CH_3 \xrightarrow{\kappa_2} CH = C - CH = CH_2 + H_2$$
 (2)

$$CH_3 \cdot + C_6H_5CH_3 \longrightarrow CH_4 + C_6H_5CH_2 \cdot$$
(3)

$$CH = C - CH_2 \cdot \longleftrightarrow CH_2 = C = CH \cdot$$
 (4)

$$CH \equiv C - CH_2 \cdot + C_6 H_5 CH_3 \longrightarrow CH \equiv C - CH_3 + C_6 H_5 CH_2 \cdot (5)$$

$$CH_2 = C = CH \cdot + C_6H_5CH_3 \longrightarrow CH_2 = C = CH_2 + C_6H_5CH_2 \cdot (6)$$

$$^{2} C_{3}^{H}_{3} \cdot \longrightarrow C_{6}^{H}_{6}$$
 (7)

$$c_{3}^{H_{3}} \cdot + c_{6}^{H_{5}CH_{2}} \cdot \longrightarrow c_{6}^{H_{5}CH_{2}} c_{3}^{H_{3}}$$

$$(8)$$

$$2 c_{6}^{H_{5}CH_{2}} \cdot \longrightarrow (c_{6}^{H_{5}CH_{2}} c_{3}^{H_{3}})$$

$$(9)$$

$${}^{2} \circ_{6^{H}5} \circ_{H_{2}} \circ \longrightarrow (\circ_{6^{H}5} \circ_{h_{2}})_{2}$$

$$\tag{9}$$

It was shown that the rate of production of $(H_2 + CH_4)$ represented adequately the over-all rate of the homogeneous, first-order disappearance of 1-butyne. The rate of formation of methane was considered to be a measure of reaction (1) which was found to be first-order with respect to 1-butyne. The activation energy of this reaction was calculated as 67 ± 2 kcal/mole and the corresponding frequency factor in the Arrhenius equation was 1.4 x 10^{14} sec⁻¹. Making the usual assumption that the recombination of free radicals requires no activation energy, the value of 67 ± 2 kcal/mole was identified with $D(CH; C \cdot CH_2 - CH_3)$. Sample Calculation (e.g. Experiment #77) Millimoles of toluene flowing through in 14 min = 79.23

Willimoles of toluene flowing through per min = $n_1 = 5.659$ Willimoles of 1-butyne flowing through in 10 min =

$$\frac{PV}{RT} \times 1000 = \frac{1.78 \times 1.183}{76 \times 0.082 \times 302.1} \times 1000 = 1.12,$$

where P is the pressure change in the storage bulb in cm, V is the volume of the storage bulb in l, T is room temperature in ^{O}K .

Millimoles of 1-butyne flowing through per min = $n_2 = 0.112$ The partial pressure of 1-butyne is then $\frac{n_2}{n_1 + n_2} \ge P$

$$= \frac{0.112}{5.659 \times 0.112} \times 1.59 = 0.03 \text{ cm}$$

where P is the pressure in the reaction vessel in cm. Total number of millimoles of gas flowing through per second

= n =
$$\frac{n_1 + n_2}{60}$$
 $\frac{5.659 + 0.112}{60}$ = 0.0962
Volume of gas flowing through per second = $\frac{nkT}{T}$
= $\frac{0.0962 \times 76 \times 0.032 \times 1018}{1.59}$ = 384.55 cc/sec
1.59
where T is the temperature of the reaction vessel in ⁰K.
The reaction time in seconds = $\frac{Volume \text{ of reaction vessel}}{Volume \text{ of gases flowing through/sec}}$
= $\frac{201.5}{384.6} \frac{\text{cc}}{\text{cc/sec}}$ = 0.53
Weight of dibenzyl = 0.01638 gm \pm 0.090 millimoles.
Total yield of non-condensibles = 0.370 millimoles.
Total yield of non-condensibles = 0.370 millimoles.
 $\frac{9}{6} \text{ CH}_4 = 67.14$
 $\frac{9}{7} \text{ H}_2 = 32.86$
millimoles of $\text{CH}_4 = 0.249$
Millimoles of $\text{H}_2 = 0.122$
Non-condensibles due to the decomposition of toluene itself = 0.032.
Millimoles of GH_4 due to toluene decomposition = $\frac{2}{5} \times 0.032 = 0.013$
Millimoles of Gh_4 due to 1-butyne decomposition = 0.249 - 0.013 = 0.236
Millimoles of H_2 due to 1-butyne decomposition = 0.224 - 0.013 = 0.236

Corrected % CH₄ = $\frac{0.236}{0.236 + 0.103}$ x 100 = 69.7

date constants:

$$k = \frac{1}{t} \frac{\ln a}{a - x} =$$

$$\frac{1}{0.53} \times 2.303 \log \frac{1.12}{1.12 - 0.339} = 0.63 \text{ sec}^{-1}$$

$$k_{1} = \frac{k(CH_{4})}{(1 - butyne)(1 - e^{-kt})} =$$

$$\frac{0.63 \times 0.236}{1.12 \times (1 - e^{-0.029 \times 0.525})}$$

$$= 0.47 \text{ sec}^{-1}.$$

$$k_{2} = k - k_{1} = 0.63 - 0.47 = 0.16 \text{ sec}^{-1}.$$

1,2 BUTADIENE

Froducts and Results

The pyrolysis of 1,2 butadiene was studied in temperature range 688-810°C. The main non-condensible product was methane. Smaller amounts of hydrogen were also formed. The proportion of methane and hydrogen varied with temperature. At the lowest temperature used for the decomposition (688°C) about 70% of the non-condensible products was methane while at the highest temperature used (S10°C) the methane was about 55% of the non-condensible gases. The yields of hydrogen and methane are shown in Table I, page 95.

The separation of the condensible products was done exclusively by means of the gas chromatography apparatus described previously and they were identified by their infrared spectra, except where indicated otherwise. Both allene and propyne were found amongst the reaction products. The ratio of the amounts of propyne to allene produced in this reaction was as in the case of 1-butyne approximately 3/2as estimated from the area under the gas chromatogram. The amount of allene plus propyne was much less than the amount of methane formed. At the highest temperature used for the decomposition (810° C) the ratio of (allene plus propyne)/CH₄ was estimated to be about 1/6; at the lowest temperature (688° C) this ratio appeared to be lower but in view of the large errors involved in determining the area of small gas

<u>Table I</u>

Products from and rate constants for the Decomposition of 1,2 Butadiene

171		L.	1 ~	- "I"
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Froducts of the Decomposition of 1,2 Butadiene

Expt NO	T ^o ĸ	Total press cm	Partial press toluene cm	Partial press 1,2 But cm	t sec	l,2 But m.moles [#]	Non- cond gases m.moles	7 ℃ H	ыb/СН ₄	k _l sec-l	k ₂ sec-1
2	961.5	1.23	1.17	0.06	0.28	4.926	0.058	70.8	13.2	0.03	0.01
9	965.5	1.30	1.27	0.03	Ú.30	3.170	0.042	70.0	-	0.04	0.01
30	969.5	1.96	1.92	0.04	1.11	0.979	0.079	60.0	-	0.05	0.03
29	975.5	1.99	1.82	0.17	1.15	2.382	0.260	62.4	27.3	U.U6	0.04
19	984.5	1.15	1.12	0.03	0.31	2.674	0 . 070	68.0	-	0.06	0.03
3	985.5	1.25	1.22	0.03	0.31	1.877	0.060	63.5	24.1	0.06	0.04
33F	986	2.08	2.04	0.04	1.16	1.205	U.136	63.7	-	0.07	Ü.U4
10	990.5	1.35	1.31	0.04	0.26	2.216	Ú.Ú82	66.2	11.0	0.11	0.04
8	990.5	1.44	1.42	0.02	0.32	1.943	0.063	68.0	-	0.08	0.04
18	994.5	1.29	1.24	0.05	0.31	1.938	0.056	74.9	18.7	0.07	0.02
20	997	1.42	1.34	0.08	0.52	1.776	0.135	63.5	15.5	0.10	0.06

* Total amount of 1,2 Butadiene flowed through during time of experiment.

Table 1 (Continued)

Expt No	$T^{O_{\vec{K}}}$	Total press cm	Partial press toluene cm	Partial press 1,2 But cm	t sec	l,2 But m.moles ^x	Non- cond gases m.moles	γ₀CH 4	[%] Dib/CH 4	k _l sec-l	k ₂ sec-l
17	992	1.26	1.23	0.03	0.31	1.983	0.074	69.9	15.8	0.09	0.04
21	1000.5	1.45	1.38°	0.07	Ú.45	2.263	0.273	58.6	15.5	0.17	0.12
25	1000.5	1.85	1.80	0.05	1.11	U.734	0.191	63.9	30.9	0.17	0.10
32P	1010	1.85	1.80	0.05	1.20	0.839	0.242	58.5	-	0.16	0.11
4	1023.5	1.30	1.27	0.03	0.30	1.995	0.149	63.1	38.4	0.16	U.10
Ĵ	1024.5	1.45	1.40	0.05	0.26	1.859	0.178	62.4	22.4	Ú.24	0.15
31P	1029	1.99	1.91	0.08	1.45	0.787	0.391	59.8	_	0.28	0.19
5	1030	1.45	1.4Ŭ	Û.Ü5	U. 29	1.246	0.148	63.2	18.9	U.28	0.16
23	1031	1.60	1.54	0.06	0.46	1.305	0.240	65.0	29.1	0.28	0.16
6	1033.5	1.29	1.23	0.06	0.27	1.267	0.185	61.1	20.5	0.36	0.23
22	1035	1.63	1.54	0.09	U. 48	1.133	0.295	60.8	-	0.38	Ŭ.24
13	1039.5	1.23	1.20	0.03	U. 29	1.790	0.253	66.4	32.1	0.36	0.18
24	1040	1.66	1.59	0.07	U.45	1.405	0.369	61.5	46.0	0.42	U.20
26	1045	2.14	2.02	U.12	1.04	0.770	0.454	57.1	-	U.49	U.37

Table I (Continued)

Expt No	$T^{O_{\overline{K}}}$	Total press cm	Partial press toluene cm	Partial press 1,2 But cm	t sec	l,2 But m.moles ^x	Non- cond gases m.moles	^{,,,0011} 4	'n Dib∕CH ₄	k _l sec-l	k ₂ sec-1
16	1045	1.22	1.18	0.04	U.29	1.977	0.324	64.7	35.3	0.40	0.24
27	1049	2.11	2.01	0.10	1.02	0.080	∪.393	63.9	-	U.53	0.30
14	1054.5	1.24	1.21	0.03	U.29	0.044	0.136	58.5	46.8	0.47	0.34
34F	1058	1.98	1.93	0.05	1.13	0.440	0.309	54.7	-	0.57	0.47
15	1067	1.19	1.17	0.02	U.26	0.700	0.198	65.2	54.4	0.84	0.46
7	1068.5	1.24	1.14	0.10	0.26	0.532	U.1 36	57.1	-	0.66	0.50
11	1069.5	1.22	1.20	0.02	0.30	0.904	Ú.21Ó	62.5	-	0.56	0.34
28	1073.5	2.04	1.97	0.07	1.04	0.369	0.320	52.2	-	1.01	0.93
12	1083.5	1.25	1.23	0.02	0.23	0.431	0.207	51.2	-	1.15	1.09

chromatographic peaks this could not be established accurately.

Large amounts of vinyl acetylene were produced in the decomposition. As in the case of 1-butyne, the amount of vinyl acetylene was usually larger than 70% of the hydrogen formed. This represents only a lower limit of the amount of vinyl acetylene formed in the reaction since some of this compound could not be readily separated from the toluene. As will be snown later, on the basis of the proposed mechanism for the pyrolysis of 1,2 butadiene it is reasonable to suggest that in actual fact the amount of vinyl acetylene was equal to the amount of hydrogen formed.

As in the pyrolysis of 1-butyne a compound with a mass of 78 was separated out on the gas chromatography column containing Apiezon L grease. The determination of its mass was made by mass spectrometry. Since the elution time for this compound was not the same as that for benzene it can be concluded that this compound was not benzene.

The yields of dibenzyl produced also in this decomposition were low, varying from about 10-54% of the methane produced (Table I). At the higher temperatures used in these experiments the dibenzyl was again slightly yellow coloured.

Trace amounts of ethane were also formed and, as in the case of the pyrolysis of 1-butyne, the amount of ethane never exceeded 1% of the amount of methane formed. Consequently, the amount of ethane formed was neglected for the calculation

96.

of rate constants.

Fost of the products from the decomposition of 1,2 butadiene are thus similar to those obtained from the decomposition of 1-butyne. However, the decomposition of 1,2 butadiene led also to the formation of 1,3 butadiene which was absent in the pyrolysis of 1-butyne. The amount of 1,3 butadiene formed at the highest temperatures used for the pyrolysis (810° C) was estimated to be of the same order of magnitude as that of the methane formed. The amount of 1,3 butadiene formed decreased rapidly with decrease in temperature. At the lowest temperature employed in this study (688° C) the amount of 1,3 butadiene formed was almost negligible.

DISCUSSION

Mechanism of Decomposition

These results suggest that 1,2 butadiene decomposes, as 1-butyne, by two simultaneous, rate determining reactions

$$CH_2 = C = CH - CH_3 \xrightarrow{\kappa_1} CH_2 = C = CH \cdot + CH_3 \cdot$$
(1)

$$CH_2 = C = CH_2 CH_3 \xrightarrow{\kappa_2} CH \equiv C - CH = CH_2 + H_2$$
(2)

and that, in addition, a third process, the isomerization of 1,2 butadiene to 1,3 butadiene occurs:

$$CH_2=C=CH-CH_3 \xrightarrow{\kappa_3} CH_2=CH-CH=CH_2$$
(3)

Reactions of the Methyl Radicals

The methyl radicals generated in step (1) are removed by the fast reaction with toluene to give methane and a benzyl radical:

$$CH_3 \cdot + C_6H_5CH_3 \longrightarrow CH_4 + C_6H_5CH_2 \cdot$$
(4)

From a study of the thermal decomposition of acetone by the toluene carrier technique, Szwarc and Taylor (90) concluded that toluene is not a sufficiently effective trap for methyl radicals, and they speculated that at 781°C about 25% of the methyl radicals formed in the decomposition might have been removed by combination with benzyl radicals:

 $CH_3 \cdot + C_6H_5CH_2 \cdot \longrightarrow C_6H_5CH_2CH_3$ (5) Experimental proof for the occurrence of reaction (5) at a temperature about $100^{\circ}C$ lower than used in the present study was obtained recently in this laboratory (91). For this purpose a technique was developed to separate ethyl benzene from a large excess of toluene. The details of the procedure used are given below.

In the standardization of this procedure it was shown that the smallest detectable concentration of ethyl benzene in toluene with the gas chromatographic apparatus was 0.2 mole %. Since its actual concentration amongst the products was expected to be still lower than that, a modified procedure, in which most of the toluene was initially removed by fractional distillation, had to be used. Portions of 5 cc of different synthetic mixtures of ethyl benzene in toluene, ranging from 0.04 to 0.1%, were degassed in the usual way and connected evacuated trap kept at liquid air temperature. Most of the toluene distilled over in 30 minutes. The last few drops remaining in the first trap were separated on the

Apiezon L grease column described previously. The contents of the trap at -78°C collected during an actual experiment were treated in an identical manner, and the chromatographic pattern obtained was compared with those given by the standard solutions. Using this technique, no ethyl benzene was detected in the present investigation. The discrepancy between the present findings and those obtained by Vrbaski et al (91) might be due to the difference in temperature in these two independent investigations since the activation energy for reaction (3) is 8.3 kcal/mole (92). Moreover the absence of ethyl benzene in this investigation may be due to the lower concentration of benzyl radicals produced in the present system, since some of them, as shown later, are removed by reactions with C_3H_3 radicals. The absence of ethyl benzene in the present study may also be ascribed to the removal of methyl radicals by the back-reaction with C_3H_3 radicals:

$$CH_3 \bullet + CH \equiv C - CH_2 \bullet \longrightarrow CH \equiv C - CH_2 - CH_3$$
 (6a)

$$CH_3 + CH_2 = C = CH + \longrightarrow CH_2 = C = CH - CH_3$$
 (6b)

According to this possibility one would expect that 1-butyne would be a product in the pyrolysis of 1,2 butadiene, and similarly 1,2 butadiene would be formed in the pyrolysis of 1-butyne. However in spite of careful gas chromatographic analyses of the products in these two reaction systems, these alternate products were not detected and therefore it can be concluded that the back reaction (6a and 6b), if any, was not significant.

99.

Fate of the Allenyl Radical

As previously shown in the introductory section, the C_3H_3 radical can be considered to resonate between the allenyl and propargyl configurations:

$$CH_2 = C = CH \cdot \longleftrightarrow CH \equiv C - CH_2 \cdot \tag{7}$$

The products formed in this pyrolysis demonstrated as in the case of the decomposition of 1-butyne, that the $C_3\pi_3$ radical can react both as a propargyl and an allenyl radical, i.e.

$$CH \equiv C - CH_2 \cdot + C_6 H_5 CH_3 \longrightarrow CH \equiv C - CH_3 + C_6 H_5 CH_2 \cdot (8)$$

$$CH_2 = C = CH \cdot + C_6 H_5 CH_3 \longrightarrow CH_2 = C = CH_2 + C_6 H_5 CH_2 \cdot (9)$$

The ratio of propyne to allene formed was again 3/2 under varying conditions of temperature. These results demonstrate again that the propargyl configuration is slightly favoured for the C_3H_3 radical (the properties of the C_3H_3 radical have been discussed in greater detail in the previous section dealing with 1-outyne).

The amount of propyne plus that of allene formed would be expected to be equal to the amount of methane produced if all the C_3H_3 radicals reacted via reactions (8) and (9). But since the amount of propyne plus allene was only about 1/6 of the methane generated at 810° C it can be concluded that the C_3H_3 radical is reluctant to abstract hydrogen atoms from toluene and that it disappears by other reactions such as its dimerization or its combination with benzyl radicals:

$$2 c_{3}H_{3} \cdot \longrightarrow c_{6}H_{6} \tag{10}$$

$$c_{3}^{H_{3}} \cdot + c_{6}^{H_{5}} c_{H_{2}} \cdot \longrightarrow c_{6}^{H_{5}} c_{H_{2}}^{H_{3}} c_{3}^{H_{3}}$$
(11)

Reaction (10) was confirmed experimentally; the pressure of a compound of mass 78 (other than benzene) was confirmed by mass spectrometry. Since the type of compound generated in reaction (11) would be expected to trap together with the toluene, no attempt was made to isolate it. Nevertheless, supporting evidence for such a reaction can be found in the low yields of dibenzyl. Also mass spectrometry has indicated that such a compound may have been actually formed in the pyrolysis of 1-butyne.

nydrogen Producing Step

The hydrogen produced in the reaction could be accounted for by reaction (2). As in the case of 1-butyne the amount of vinyl acetylene formed was considered to be equal to the amount of hydrogen formed. The possibility that hydrogen is produced via a free radical process,

$$CH_2 = C = CH_2 - CH_3 - CH_3 - CH = C = CH + H + (12)$$

$$CH_{3}-CH=C=CH \cdot \longrightarrow CH_{2}=CH-C\equiv CH + H \cdot$$
 (13)

was ruled out for the same reasons as given in the case of 1-butyne. Moreover the conclusions of the study of the mercury photosensitized decomposition of 1,2 butadiene by Collin and Lossing (83) are particularly adequate for the discussion of the present results. In the latter study the reactant and products were sampled directly into the ionization chamber of a mass spectrometer. Collin and Lossing stated that the $C_{\mu}H_5$ radical was not detected by mass spectrometry and that a compound with a mass of 52, presumably vinyl acetylene was formed. However they detected the formation of the $C_{3}H_{3}$ radicals. These results are therefore consistent with those obtained in the present study. In general there may not be a correlation between the mechanisms of a thermal and a mercury photosensitized decomposition in as much as the energization step(s) leading to reaction may be different^{*}. However the similarity of the products formed in both this study and that of Collin and Lossing, which can be accounted for by reactions (1) and (2) would support the view that the same mechanism underlies both decompositions.

x In this connection it might be worth mentioning that most mercury photosensitized decompositions of hydrocarbons involve the fission of only one C-H bond by a free radical mechanism (70).

Formation of dibenzyl

The formation of dibenzyl is accounted for by the dimerization of benzyl radicals, presumably outside the reaction zone proper:

$$2 \ C_6 H_5 CH_2 \cdot \longrightarrow (C_6 H_5 CH_2)_2 \tag{14}$$

The low yields of dibenzyl can be explained in the same manner as that proposed for the pyrolysis of 1-butyne. It has been shown that the C_3H_3 radical is relatively stable and reluctant to abstract a hydrogen atom from toluene (reactions 6 and 9) and in consequence it is likely that the concentration of C_3H_3 radicals is larger than that of the CH_3 radicals produced in reaction (1). As a result of this the yield of benzyl radicals is low. Moreover since it is likely that benzyl radicals may combine with C_3H_3 radicals, the concentration of benzyl radicals is further reduced, resulting in the low yields of dibenzyl. This explanation would also account for the absence of ethylbenzene amongst the products and thus one must conclude that reaction (5) does not occur.

Formation of 1,3 butadiene

Various amounts of 1,3 butadiene, accounted for by reaction (3), were found amongst the reaction products. At low temperatures, only a negligible amount of 1,3 butadiene was formed. The ratio of 1,3 butadiene to methane increased with increasing temperature, and at the highest temperature used (811°C) the amount of 1,3 butadiene formed was estimated to be equal to the amount of methane formed. This would indicate that the isomerization[#] of 1,2 butadiene to 1,3 butadiene requires a substantial activation energy.

In the study of the mercury photosensitized decomposition of 1,2 butadiene by Collin and Lossing (83) no mention was made of the presence of 1,3 butadiene amongst the products of reaction. Nevertheless in their study of the mercury photosensitized decomposition of 1,3 butadiene (83), 1,2 butadiene was proposed as a product. A large amount of 1-butyne was also formed as a product in the mercury photosensitized decomposition of 1,3 butadiene; therefore the identification of 1,2 butadiene in the presence of both 1,3 butadiene and 1-butyne was not unambiguous. Since 1-butyne was also formed as a product in the mercury photosensitized decomposition of 1,2 butadiene the detection of 1,3 butadiene as a product may have been obscured.

It is of interest to see how 1,3 butadiene behaved in the present reaction system. Consequently a few experiments were made using 1,3 butadiene (Matheson, research grade) under conditions identical to those used for 1,2 butadiene.

104.

^{*} This isomerization (reaction 3) is exothermic to the extent of 12.4 kcal/mole. $\Delta h_{f}(1,2 \text{ butadiene}) = 38.77 \text{ kcal/mole}, \Delta H_{f}(1,3 \text{ butadiene})$ = 26.33 kcal/mole (82).

The extent of decomposition of 1,3 butadiene was estimated to be only a small fraction of the extent of decomposition of 1,2 butadiene. No extensive studies were made with 1,3 butadiene and therefore no kinetic data can be derived from the pyrolysis of this compound. The non-condensible products consisted of methane and hydrogen, and the ratio of CH_{L}/H_{2} was slightly lower in the case of 1,3 butadiene. Again both propyne and allene were found as reaction products, and the ratio of propyne to allene was about 3/2. Small amounts of 1,2 butadiene were also found. These results indicate that the conversion of 1,3 butadiene to 1,2 butadiene is slow under the conditions used for the pyrolysis of the latter, and that the other products formed are a result of the subsequent pyrolysis of 1,2 butadiene. This explanation is also consistent with the mechanism proposed by Collin and Lossing (83) and the hydrogen snift involved in these isomerizations is illustrated in the diagram given below.



105.

Summary of mechanism

The overall mechanism for the pyrolysis of 1,2 butadiene in a stream of toluene can then be summarized in terms of the following reactions:

$$CH_2 = C = CH - CH_3 \xrightarrow{k_1} CH_2 = C = CH \cdot + CH_3 \cdot (1)$$

$$CH_2 = C = CH - CH_3 \xrightarrow{K_2} CH C - CH = CH_2 + H_2$$
 (2)

$$CH_2 = C = CH - CH_3 \xrightarrow{\kappa_3} CH_2 = CH - CH = CH_2$$
 (3)

$$cH_3 \cdot + c_6H_5CH_3 \longrightarrow cH_4 + c_6H_5CH_2 \cdot$$
(4)

$$CH_2 = C = CH \cdot \longleftrightarrow CH \equiv C - CH_2 \cdot \tag{7}$$

$$CH_2 = C = CH \cdot + C_6H_5CH_3 \longrightarrow CH_2 = C = CH_2 + C_6H_5CH_2 \cdot (8)$$

$$CH \equiv C - CH_2 \cdot + C_6 H_5 CH_3 \longrightarrow CH \equiv C - CH_3 + C_6 H_5 CH_2 \cdot$$
(9)
2 C_2 H_2 \cdot \longrightarrow C_6 H_6 (10)

$$c_{3}H_{3} \cdot \longrightarrow c_{6}H_{6} \tag{10}$$

$$c_{3}H_{3} \cdot + c_{6}H_{5}CH_{2} \cdot \longrightarrow c_{6}H_{5}CH_{2}C_{3}H_{3}$$
(11)

$$2 \circ_{6^{H_{5}CH_{2}}} \longrightarrow (\circ_{6^{H_{5}CH_{2}}})_{2}$$
(14)

Kinetic considerations

To obtain the carbon-carbon bond dissociation energy in 1,2 butadiene, D(CH₂:C:CH-CH₃), values for the rate constant k₁ are required over a range of temperature. The methane produced in reaction (4) measures the extent of reaction (1), i.e.

$$\frac{d(CH_4)}{dt} = k_1(B)$$

where (B) represents the concentration of 1,2 butadiene. However, according to the postulated mechanism the 1,2 butadiene disappears simultaneously by the three unimolecular processes, reactions (1), (2) and (3) and therefore one may

write

$$-\frac{d(B)}{dt} = (k_1 + k_2 + k_3) (B)$$
$$= k_0 (B)$$

where k_0 is the rate constant for the overall removal of 1,2 butadiene. Upon integration of this expression (between zero time and time t) the following expression is obtained:

$$k_{o} = \frac{2.303}{t} \log \frac{(B)_{o}}{(B)_{t}}$$

or
$$(B)_{t} = (B)_{o} e^{-k_{o}t}$$

Hence,

$$\frac{d(CH_{4})}{dt} = k_{1}(B)_{0}e^{-k_{0}t}$$

which upon integration gives:

$$k_{1} = \frac{k_{o}(CH_{4})o}{(B)_{o}(1 - e^{-k_{o}t})}$$

Consequently, in order to calculate k_1 at any temperature, an estimate must first be made of the overall rate constant, k_0 . In theory the overall rate constant k_0 may be calculated from the amount of 1,2 butadiene consumed during the reaction, or it may also be estimated from the rate of formation of the sum of metnane, hydrogen and 1,3 butadiene. But due to technical reasons k_0 was not easily obtained. The amount of unreacted 1,2 butadiene could not be estimated accurately due to the difficulty of separating it from the large excess of toluene and due to the difficulty encountered in trying to measure accurately the amount of 1,3 butadiene formed in the reaction.

Nevertheless, calculations were made on this system by neglecting reaction (3), i.e. assuming $k_3 = 0$. The overall rate constant, k, can then be written as

$$k = k_1 + k_2 = \frac{2.303}{t} \log \frac{(B)_0}{((B)_0 - (CH_4 + H_2))}$$

Assuming then that the methane formed in the reaction resulted from the reaction of CH_3 radicals generated in reaction (1) only, the rate constant k_1 can be represented as follows:

$$k_{1} = \frac{k(CH_{4})_{0}^{t}}{((B)_{0}(1 - e^{-kt}))}$$

The values of k_1 shown in Table I, page 95 were calculated in this manner. These rate constants were found to be insensitive to changes in toluene pressure, partial pressure of 1,2 butadiene and time of contact. This is illustrated in Tables II, III and IV, pages 109, 110 and 111, respectively. The effect of variation of surface/volume ratio on k_1 is shown in Table V, page 112. The values of k_2 , shown in Table I, was calculated from the expression:

 $k_2 = k - k_1$

Calculation of activation energies

A plot of log k_1 vs. 1/T is shown in Fig. 11, page 113. From the slope of this line an activation energy of 66 \pm 2

Table II

Effect of deaction Time on First-Order date Constant, \boldsymbol{k}_{l}

Expt No	$T^{O_{\overline{K}}}$	Time of Contact	k _l sec-l		
annyen den an night de Staft age				^k 965.5	-
9	965.5	0.30	0.04	0.04	
30	969.5	1.11	0.05	0.04	
				^k 1000.5	
21	1000.5	0.45	0.17	0.17	
25	1007	1.11	0.17	0.16	
				^k 1030	
5	1030	0.29	0.28	0.28	
23	1031	0.46	0.28	Ŭ.27	
				^k 1039.5	
13	1039.5	0.29	0.36	0.36	
24	1040	0.45	0.42	0.42	
				^k 1045	
16	1045	0.29	0.40	0 . 40	
27	1049	1.02	0.53	0.47	

<u>Table III</u>

	on First-Order date Constant, k _l						
Expt No	т ^о к	l,2 Butadiene Fress cm	kl sec-l				
				k _{965.5}			
9	965.5	0.03	0.04	0.04			
2	961.5	0.06	0.03	0.03			
				^k 969.5			
30	969.5	0.04	0.05	0.05			
29	975.5	0.17	0.06	0.05			
				^k 1030			
5	1030	0.05	0.28	0.28			
23	1031	U.06	Ú.28	0.27			
				^k 1039.5			
13	1039.5	0.03	0.36	0.36			
24	1040	0.07	0.42	0.42			
				^k 1083.5			
12	1083.5	0.02	1.15	1.15			
28	1073.5	0.07	1.01	1.25			

Effect of Partial Pressure of 1,2 Butadiene on First-Order Mate Constant, k₁

Table IV

		tate Constant	t ^k l	5-01461
Expt No	TOK	Toluene press cm	kl sec-l	
				^k 965.5
9	965.5	1.27	0.04	0.04
30	969.5	1.92	0.05	0.04
				^k 1000.5
21	1000.5	1.38	0.17	0.17
25	1007	1.80	0.17	0.16
				k _{1033.5}
6	1033.5	1.29	0.36	0.36
22	1035	1.63	0.38	0.36
				k _{10/0}
24	1040	1.59	0.42	0.42
26	1045	2.02	0.49	0.42
				k ₁₀₄₅
16	1045	1.18	0.40	0.40
17	1049	2.01	Ű.53	0.47

Effect of Toluene Fressure on First-Order

Effect of Facked Reaction Vessel on First-Order Rate Constant, k						
Expt No	T ^o k	kl sec-l				
			^k 985.5			
3	985.5	0.06	0.06			
33F	986	0.07	0.07			
			^k 1030			
5	1030	0.28	Ũ.28			
31 F	1029	0.28	Ú.29			
			^k 1007			
25	1007	Ü.17	0.17			
32P	1010	0.16	0.14			
			^k 1054.5			
14	1054.5	0.47	0.47			
34P	1058	0.57	0.51			

<u>Table V</u>

Figure 11

Plot of log k_1 vs. 1/T

Filled circles denote experiments done in packed vessel



kcal/mole was calculated for reaction (1) in the same manner previously described in the corresponding section for 1-butyne. Also the discussion relating to the errors involved and presented in that section is equally applicable to this case. The frequency factor in the Arrhenius expression was calculated as $3.6 \times 10^{13} \text{sec}^{-1}$.

This activation energy of 66 ± 2 kcal/mole cannot be considered to be absolutely correct since it was derived by neglecting reaction (3) which was responsible for the formation of 1,3 butadiene, i.e. the assumption was made that $k_3 = 0$. As stated previously, at the lowest temperatures the amount of 1,3 butadiene formed was negligible and therefore at these temperatures k_1 was much greater than k_3 . Consequently the error made in calculating \boldsymbol{k}_{γ} at these temperatures is insignificant. But with increase in temperature the ratio of 1,3 butadiene to CH_{L} formed increased and therefore k_3 should no longer be neglected in the calculation of k_1 . The amount of 1,3 butadiene formed at the highest temperature (810°C) was estimated to be of the same order of magnitude as the methane formed. Taking into account this additional reaction (3) the value of the rate constant k_1 at 810° C is increased from 1.15 sec⁻¹ to 1.56 sec⁻¹. Thus even at the highest temperature used in this decomposition the rate constant is increased only by about 35%. The log of this rate constant was plotted on the graph of log $k_{\rm l}$ vs. l/T

and was extrapolated back to the lowest temperature as shown by the dashed line in Fig. 11, page 113. The value of the activation energy calculated from the slope of this line is 65 kcal/mole. This value represents a maximum for the activation energy since, even at the lowest temperature, k3 is not quite equal to zero, and therefore the dashed line should theoretically not intersect the line of $\log k_1$ vs. 1/T at the lowest temperature. Strictly speaking the plot of log k_1 vs. 1/T should show some curvature, but since this could not be ascertained because of the scatter of the experimental data a straight line was drawn. It is felt that a line of intermediate slope would represent more adequately the true activation energy and therefore, the activation energy of reaction (1) may be considered to be equal to 67 + 2kcal/mole (i.e. intermediate between 66 kcal/mole and 68 kcal/mole).

A plot of log k_2 vs. l/T is shown in Fig. 12, page 116^{\times} . It is evident that the increase in surface/ volume ratio by a factor of 14 had no effect on reaction (2). The slope of this line corresponds to an activation energy of $80\pm$ (?) kcal/mole. The frequency factor in the Arrhenius equation was calculated as $1.5 \times 10^{16} \text{sec}^{-1}$. Taking into account the amount of 1,3 butadiene formed in the pyrolysis

115.

^{*} The k₂ values were calculated on the assumption that reaction (3) did not occur.

Figure 12

Plot of log k_2 vs. l/T

Filled circles denote reactions done in packed vessel



at 810° C the rate constant k_2 is increased from 1.09 to 1.49 sec⁻¹. The log of this latter value was plotted on the log k_2 vs. L/T graph and was extrapolated as shown by the dashed line in Fig. 12, page 116. The value of the activation energy calculated from the slope of the dashed line is 83 kcal/mole. As above, one may therefore consider the activation energy of reaction (2) to be within the range 80-63 kcal/mole.

Conclusions

It is considered that the rate of production of $(GH_4 + H_2 + GH_2 = GH - GH = GH_2)$ represents adequately the overall rate of the homogeneous first-order disappearance of 1,2 butadiene. Because of the technical problems involved in estimating accurately the condensible products formed, the rate of formation of 1,3 butadiene was initially neglected in the calculations used for the evaluation of the rate constant of reaction (1) and the value of 60 \pm 2 kcal/mole was deduced for the activation energy of this reaction. However on taking into account the rate of formation of 1,3 butadiene the activation energy of reaction (1) was estimated as 67 \pm 2 kcal/mole which is identified with D(GH₂:C:CH-CH₃).

GENERAL DISCUSSION

valculation of dissociation energies

The relation between the experimental activation energy for a unimolecular reaction, involving the decomposition of a molecule into two radicals, and the dissociation energy of the bond which is broken has been discussed. It was concluded that $D + RT \rangle E \rangle D$, where D is the dissociation eneray at 0°k. For most compounds, for which the preexponential term in the Arrhenius rate expression is close to 10¹³sec⁻¹, the measured activation energy was considered to be very nearly equal to D. To compute the heats of formation of free radicals using standard reference neats of formation at 25° , the activation energy for the relevant dissociation processes ought to be calculated for 25°C also. This may be done as suggested by Trotman-Dickenson (93) by considering only the increase in translational degrees of freedom resulting from the increase in the number of particles of dissociation. Since the molecule is changed only by the rupture of one bond, the change in the specific heats arising from vibrational and rotational terms may be neglected. On this basis the measured activation energies should be increased by 3/2 RT. However this correction is of the same order of magnitude as the uncertainty of the order of RT mentioned above. In view of this and the experimental errors involved this correction has been neglected. Therefore, the measured
activation energies were used together with appropriate heats of formation at 25°C in calculations of the heats of formation of free radicals.

It was shown previously that if the $C_{3}h_{3}$ radical generated from the pyrolysis of either 1-butyne or 1,2 butadiene can be considered to be an identical species, the difference between the C-C bond dissociation is given by the relation

 $\Delta D = \Delta H_f(1-butyne) - \Delta H_f(1,2 butadiene) = 0.7 kcal/mole$ The values derived for the two C-C bond dissociation energies in the present study were identical within the accuracy of the method used, i.e. $\Delta D = 0$. This agreement between the experimentally determined difference in C-C bond dissociation energies and that obtained from thermochemical data is good considering the assumptions made in the two mechanisms and the errors associated with the analytical procedures used for the quantitative determination of the C_L hydrocarbons.

The heat of formation of the C_3H_3 radical can be calculated from two independent sets of data:^{*} (1) $\Delta H_f(C_3H_3) = D(CH_1^*C \cdot CH_2 - CH_3) + \Delta H_f(CH_1^*C \cdot CH_2 \cdot CH_3) - \Delta H_f(CH_3)$ = 67 + 39.5 - 32.0 = 74.5 kcal/mole (2) $\Delta H_f(C_3H_3) = D(CH_2 \cdot C \cdot CH_3) + \Delta H_f(CH_2 \cdot C \cdot CH_3) - \Delta H_f(CH_3)$ = 67 + 38.8 - 32 = 73.8 kcal/mole

119.

In these calculations, the following data were used: $\Delta H_{f}(CH_{3}) = 32.0 \text{ kcal/mole } (94), \Delta H_{f}(CH_{2}:C:Ch \cdot CH_{3}) = 38.77 \text{ kcal/mole}, \Delta H_{f}(CH;C \cdot CH_{2} \cdot CH_{3}) = 39.48 \text{ kcal/mole } (82).$

It would seem, therefore, reasonable to assign the average value of about 74 kcal/mole to the heat of formation of the C_3H_3 radical.

Using this value and the relevant thermodynamic data the C-C bond dissociation energies in 1-butyne and 1,2 butadiene were calculated to be 66.5 kcal/mole and 67.2 kcal/mole respectively from the two above expressions. As mentioned previously, from the electron impact data obtained for allene, propyne, 1-butyne, 1,2 butadiene and 1,3 butadiene, Collin and Lossing (85) calculated the C-C bond dissociation energy in 1-butyne, $D(CH;C:CH_2-CH_3)$, and 1,2 butadiene, $D(CH:C:CH-CH_3)$, to be 67.5 and 68.2 kcal/mole. These values are in obviously a close agreement with those obtained in the present investigation.

The C-H bond dissociation energy in propyne, $D(CH:C\cdot CH_2-H)$, can be calculated from the heats of formation of propyne and hydrogen atom, i.e.

> $D(CH; C \cdot CH_2 - R) = \Delta H_f(C_3H_3) + \Delta H_f(H) - \Delta H_f(CH; C \cdot CH_3)$ = 74 + 52.1 - 44.3 = 81.8 kcal/mole

Similarly the C-H bond dissociation energy in allene, $D(CH_2:C:CH-H)$, can be calculated by using the appropriate thermochemical relation:^x

^{*} In these calculations the following data were used: $\Delta H_{f}(H) = 52.1 \text{ kcal/mole (94), } \Delta H_{f}(Ch?C.CH_{3}) = 44.32 \text{ kcal/mole, } \Delta H_{f}(CH_{2}=C=CH_{2}) = 45.92 \text{ kcal/mole (82).}$

 $D(CH_2:C:CH-H) = \Delta H_f(C_3H_3) + \Delta H_f(H) - \Delta H_f(CH_2=C=CH_2)$ = 74 + 52.1 - 45.9 = 80.2 kcal/mole

A few remarks concerning the C-H bond dissociation energies in allene and propyne seem in order. At first sight one might expect the C-H bond in allene to be considerably stronger than in propyne since the H atom in the former case might be considered to be "ethylenic". However since the loss of a H atom from either allene or propyne results in the formation of the same free radical, and since the heat of formation of allene and propyne differ by only 1.6 kcal/mole, the difference in the bond dissociation energies of these two compounds is consequently within this range.

Resonance Energy of the C_3H_3 Radical

It was shown previously that the lowering of the R-H bond dissociation energy in the molecule RH with respect to the C-H bond dissociation energy in methane represents the resonance energy, π_{ρ} , of the radical R, i.e.

$$R_e = D(CH_3-H) - D(R-H)$$

The resonance energy of the C_3H_3 radical can hence be calculated from the values obtained for the C-H bond dissociation energies in allene and propyne respectively,

$$R_e = D(CH_3-H) - D(CH_2:CH-H)$$

= 102 - 80.2 = 21.8 kcal/mole

$$R_e = D(CH_3-H) - D(CH_2-H)$$

= 102 - 81.8 = 20.2 kcal/mole.

The difference of 1.6 kcal/mole between these two values, the correctness of which will obviously also depend on the accuracy of the relevant heats of formation used, might be interpreted as being due to the strengthening of the C-H bond in propyne relative to allene by factors such as hyperconjugation.

Stability of the C3H3 Radical

The O_3H_3 radical, as was shown earlier, is stabilized by a large experimental resonance energy which was explained as being due to the O_3H_3 radical resonating between the propargyl and allenyl configurations:

 $CH \equiv C = CH_2 \cdot \longleftrightarrow CH_2 = C = CH \cdot$

It was shown that the C_3H_3 radicals produced in the decompositions of both 1-butyne and 1,2 butadiene abstracted hydrogen atoms from toluene to yield propyne and allene,

 $\begin{array}{ccc} c_{3}H_{3} \cdot + c_{6}H_{5}CH_{3} \longrightarrow CH \equiv c_{6}CH_{3} + c_{6}H_{5}CH_{2} \cdot \\ c_{3}H_{3} \cdot + c_{6}H_{5}CH_{3} \longrightarrow CH_{2} = c_{6}CH_{2} + c_{6}H_{5}CH_{2} \cdot \end{array}$

These results are in direct conflict to those obtained from the mercury photosensitized decomposition of allene by Collin and Lossing (83). These workers concluded that the C_3H_3 radical had predominately the propargyl configuration, since the C_3H_3 radicals generated from the mercury photosensitized decomposition of allene were found to combine with methyl radicals to form primarily 1-outyne as a product. However, Srinivasan (84) has recently demonstrated that the C_3H_3 radicals generated in the photodecomposition of 1,3 butadiene dimerized to give two different products of mass 78 and has suggested that the C_3H_3 radical can exist in both the propargyl and allenyl configurations. In a very recent study by Frey (95) of the addition of methylene to allene, C_3H_3 radicals were generated in the reaction:

 $CH_2 + OH_2 = C = CH_2 \longrightarrow CH_3 + C_3H_3$. Frey assumed that the C_3H_3 radical had the propargyl configuration (this assumption was based on the conclusion of Collin and Lossing mentioned above) and explained the formation of 1-butyne in his study in terms of the reaction involving the combination of a CH_3 radical with a C_3H_3 radical. However, for the formation of 1,2 butadiene which was also produced in his system he postulated the reaction:

 $CH_2 + CH_2 = C = CH_2 \longrightarrow CH_3 CH = C = CH_2 \longrightarrow CH_3 CH = C = CH_2$ However, the results of Srinivasan (54) and those of the present work suggest that the 1,2 butadiene may have been also formed by the combination of a CH_3 radical and a C_3H_3 radical:

CH_3 . + CH_2 =C=CH. \rightarrow CH_2 =C=CH-OH₃

It is very difficult to visualize why the $c_{3}\bar{n}_{3}$ radical is stabilized to such a great extent if it existed only in the propargyl configuration. The weight of all this evidence supports therefore the view that the C3H3 radical resonates between the propargyl and allenyl forms and reacts in either configuration.

Trrespective of the source of the C_3H_3 radical (i.e. from both 1-butyne and 1,2 butadiene), the ratio of propyne to allene was 3/2. Furthermore, this ratio was found to be temperature independent over the temperature range studied. This may indicate that the interconversion from the allenyl to the propargyl configuration occurs without or with a very small activation energy and consequently the activation energy for the abstraction of a hydrogen atom from toluene by this radical is probably similar for either form. This conclusion is similar to that of Ryce and Bryce (96) who proposed that the interconversion of the butenyl radical

$CH_2=CH-CH-CH_3 \longleftrightarrow \cdot CH_2-CH=CH-CH_3$

requires an activation energy of about 1-2 kcal/mole. However, in their study the ratio of the two possible reaction products resulting from the combination of a methyl radical with a butenyl radical was 6, whereas in the present investigation the ratio of propyne/allene formed was only 3/2. Hence one may state that the interconversion between the two forms of the C_3H_3 radical would require an activation energy smaller than that postulated by these workers for the localization of the free electron in the butenyl radical. The activation energy for the reaction of a C_3H_3 radical with toluene was evaluated in the following manner. It was estimated that the ratio of $GH_4/(allene plus propyne)$ formed in the decompositions of both 1-butyne and 1,2 butadiene was 6 at the highest temperatures and therefore on the assumption that the activation energies of the reactions

$$\begin{array}{cccc} & & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & \\ & & & &$$

are identical one may write the relation:

 $\frac{\text{rate of formation of GM}_{4}}{\text{rate of formation of (allene + propyne)}} = \frac{k^{1}(GH_{3})(\text{toluene})}{k^{11}(G_{3}h_{3})(\text{toluene})} = 6$ According to the mechanism proposed, the concentration of the GH₃ radical can be considered equal to the concentration of the G₃h₃ radical to a first approximation. Therefore,

$$\frac{\mathbf{k}^{1}}{\mathbf{k}^{1}\mathbf{l}} = \frac{\mathbf{A}^{1}\mathbf{e}^{-\mathbf{E}}\mathbf{l}/\mathbf{K}^{T}}{\mathbf{A}^{1}\mathbf{l}\mathbf{e}^{-\mathbf{E}}\mathbf{l}/\mathbf{K}^{T}} = 6$$

If it is further assumed that this ratio arises solely because of the difference in activation energies for these processes,

 $E^{11} - E^{1} \simeq 3.9 \text{ kcal/mole}^{*}$

The activation energy, \mathbb{E}^1 , for the reaction of methyl radicals with toluene was estimated by Trotman-Dickenson (92) to be 8.3 kcal/mole, and hence the activation energy for the reaction

^{*} The nighest temperatures used in the decompositions of l-butyne and 1,2 butadiene were 1090 and 1083°K respectively. The average value of 1087°K was used in the calculation.

between $C_{3}H_{3}$ radicals and toluene is about 12 kcal/mole. This value is considered to be only a rough estimate in the light of the assumptions made to derive it. The true value may be greater than 12 kcal/mole since the steady state concentration of methyl radicals would be expected to be lower than that of the $C_{3}H_{3}$ radicals, which are relatively stable and probably disappear to a large extent by dimerizing and by combining with a benzyl radical in the colder regions of the reaction vessel.

It is of interest to compare the properties of the C_3H_3 radical with those of the allyl and benzyl radicals. The large resonance energy (24.5 kcal/mole) of the benzyl radical is explained by the conjugation of the p-electrons of the carbon atom of the CH_2 group with those of the carbon atoms of the ring, which results in almost complete delocalization of the electrons througnout the radical. The allyl radical has been shown to be stabilized to the same extent as the benzyl radical (25 kcal/mole). This large resonance energy for the allyl radical is acceptable since this radical may resonate between two identical structures:

 $CH_2=CH-CH_2 \leftrightarrow \rightarrow \circ CH_2-CH=CH_2$ The resonance energy of 22 kcal/mole calculated in this study for the C_3H_3 radical can be also explained on the basis of this radical resonating between the two structures

 $CH = C - CH_2 \cdot \longleftrightarrow CH_2 = C = CH \cdot$

whose energy levels are probably close together. The thermal stability of the $C_3^{H_3}$ radical is greater than that of the allyl radical even though the $C_3^{H_3}$ radical is stabilized to a lesser extent than the allyl radical. The allyl radical is capable of dissociating further and the dissociation energy, $D(CH_2:C\cdot CH_2\cdot)$, was calculated (81) as only

68.5 kcal/mole. On the other hand the C_3H_3 radical does not decompose further in the temperature range used. In this respect the C_3H_3 radical is similar to the benzyl radical and therefore it is proposed that either allene or propyne might prove suitable as radical removers. To test this hypothesis the pyrolysis of propyne was investigated in a preliminary fashion. Though sufficient results were not obtained for postulating unequivocally a mechanism for this pyrolysis, they indicate that further study is warranted. <u>Conclusions</u>

The thermal decomposition of 1-butyne, as well as of 1,2 butadiene, in the presence of an excess of toluene was found to be complicated as is evident from the mechanisms postulated for these pyrolyses. Of these two decompositions the pyrolysis of 1-butyne appeared to be the less complicated. Nevertheless, even in the study of 1-butyne, many assumptions and oversimplifications were made in arriving at a value for the C-C bond dissociation energy. Perhaps, the assumption which is most seriously open to criticism is that the hydrogen was produced by a molecular mechanism. The validity of this hypothesis was based primarily on indirect evidence.

In the study of 1,2 butadiene, the formation of 1,3 butadiene was an additional complication. The analysis for 1,3 butadiene was associated with technical difficulties. Even at the highest temperature used, where the amount of 1,3 butadiene formed was maximal, the rate constant for reaction (1) was not substantially affected when the 1,3 butadiene formed was taken into consideration. Therefore, it was felt that the rate of isomerization of 1,2 butadiene to 1,3 butadiene could be neglected for the calculation of the rate constants of reaction (1). As in the case of 1-butyne the formation of hydrogen was assumed to occur by means of a molecular mechanism. The arguments made in favour of such a mechanism were the same as those made for 1-butyne; and in addition, in support of this mechanism one could quote the independent results of Collin and Lossing's study of the mercury photosensitized decomposition of 1,2 butadiene (83). From a comparison of the structures of 1-butyne and 1,2 butadiene it is obvious that the mechanism underlying the molecular elimination of hydrogen is more complicated in the latter case.

In spite of the inability to define more precisely some of the reaction steps participating in the overall

128.

decomposition of 1-butyne and 1,2 butadiene, it is gratifying to find such a good agreement between the difference in the two C-C bond dissociation energies derived on the basis of the kinetic data presented here and their difference calculated from thermochemical data. It is difficult to see how this agreement could be simply fortuitous and one can therefore conclude that the value derived for $\Delta H_f(C_3H_3)$ is reasonably accurate and that the toluene carrier technique, in spite of its limitations provides a useful method for the calculation of bond dissociation energies.

SUMMARY AND CONTRIBUTIONS TO KNOWLEDGE

- The thermal decompositions of 1-butyne and 1,2 butadiene were studied using the toluene carrier technique.
- 2. The products of the decomposition of 1-butyne were methane, hydrogen, allene, propyne, vinyl acetylene, a C_6H_6 compound other than benzene, dibenzyl and probably a $C_{10}H_{10}$ compound, and were accounted for by the mechanism:

$$\begin{array}{c} \text{CH} \equiv \text{C}-\text{CH}_2-\text{CH}_3 \xrightarrow{k_1} \text{Ch} \equiv \text{C}-\text{CH}_2 \cdot + \text{CH}_3 \cdot \\\\ \text{CH} \equiv \text{C}-\text{CH}_2-\text{CH}_3 \xrightarrow{k_2} \text{CH} \equiv \text{C}-\text{CH}=\text{CH}_2 + \text{H}_2 \\\\ \text{CH} \equiv \text{C}-\text{CH}_2-\text{CH}_3 \xleftarrow{} \text{CH} \equiv \text{C}-\text{CH}=\text{CH}_2 \cdot \\\\ \text{CH} \equiv \text{C}-\text{CH}_2 \cdot + \text{C}_6\text{H}_5\text{CH}_3 \xleftarrow{} \text{CH} \equiv \text{C}=\text{CH} \cdot \\\\ \text{CH} \equiv \text{C}-\text{CH}_2 \cdot + \text{C}_6\text{H}_5\text{CH}_3 \xrightarrow{} \text{CH} \equiv \text{C}-\text{CH}_3 + \text{C}_6\text{H}_5\text{CH}_2 \cdot \\\\ \text{CH}_2 \equiv \text{C}=\text{CH} \cdot + \text{C}_6\text{H}_5\text{CH}_3 \xrightarrow{} \text{CH} \equiv \text{C}=\text{CH}_2 + \text{C}_6\text{H}_5\text{CH}_2 \cdot \\\\\\ \text{C}_3\text{H}_3 \cdot \xrightarrow{} \text{C}_6\text{H}_6 \\\\ \text{C}_3\text{H}_3 \cdot + \text{C}_6\text{H}_5\text{CH}_2 \cdot \xrightarrow{} \text{C}_6\text{H}_5\text{CH}_2\text{C}_3\text{H}_3 \\\\\\ \text{Z} \quad \text{C}_6\text{H}_5\text{CH}_2 \cdot \xrightarrow{} \text{C}_6\text{H}_5\text{CH}_2\text{C}_3\text{H}_3 \\\\\\ \text{Z} \quad \text{C}_6\text{H}_5\text{CH}_2 \cdot \xrightarrow{} \text{C}_6\text{H}_5\text{CH}_2\text{C}_3\text{H}_3 \\\\\end{array}$$

 The rate constant k₁ for the first-order, homogeneous decomposition of 1-butyne,

 $CH \equiv C - CH_2 - CH_3 \longrightarrow CH \equiv C - CH_2 \cdot + CH_3 \cdot$ which was measured by the rate of formation of methane over the temperature range 674-817°C was found to be represented by the expression

$$k_1 = 1.4 \times 10^{14} e^{-\frac{67.000}{RT}} sec^{-1}$$

- 4. This activation energy was identified with D(CH:C·CH₂-CH₃) and the heat of formation of the C₃H₃ radical was calculated to be 74.5 kcal/mole.
- 5. The rate constant \mathbf{k}_2 for the homogeneous decomposition of 1-butyne

 $CH=C-CH_2-CH_3 \longrightarrow CH=C-CH=CH_2 + H_2$ determined from the rate of formation of H_2 over the temperature range 674-817°C was represented approximately by the expression

$$k_2 = 10^{16} e^{-\frac{78,000}{RT}} sec^{-1}$$
.

6. The products formed in the pyrolysis of 1,2 butadiene were identical to those formed in the decomposition of 1-butyne except for the formation of 1,3 butadiene which was absent in the latter case. The following mechanism was postulated to account for the products

$$\begin{array}{c} \operatorname{CH}_{2}=\operatorname{O}=\operatorname{CH}_{\circ}\operatorname{CH}_{3} \xrightarrow{k_{1}} \operatorname{CH}_{2}=\operatorname{O}=\operatorname{CH}_{\circ} + \operatorname{CH}_{3} \cdot \\ \operatorname{CH}_{2}=\operatorname{O}=\operatorname{OH}_{\circ}\operatorname{CH}_{3} \xrightarrow{k_{2}} \operatorname{CH}=\operatorname{O}_{\circ}\operatorname{CH}=\operatorname{CH}_{2} + \operatorname{H}_{2} \\ \operatorname{CH}_{2}=\operatorname{O}=\operatorname{CH}_{\circ}\operatorname{CH}_{3} \xrightarrow{k_{3}} \operatorname{CH}_{2}=\operatorname{CH}_{\circ}\operatorname{CH}=\operatorname{CH}_{2} \\ \operatorname{CH}_{3} \cdot + \operatorname{C}_{6}\operatorname{H}_{5}\operatorname{CH}_{3} \xrightarrow{} \operatorname{CH}_{4} + \operatorname{C}_{6}\operatorname{H}_{5}\operatorname{CH}_{2} \cdot \\ \operatorname{CH}_{2}=\operatorname{O}=\operatorname{CH}_{\circ} \xleftarrow{} \operatorname{CH}=\operatorname{O}_{\circ}\operatorname{CH}_{2} \cdot \\ \operatorname{CH}_{2}=\operatorname{O}=\operatorname{CH}_{\circ} \xleftarrow{} \operatorname{CH}=\operatorname{O}_{\circ}\operatorname{CH}_{2} \cdot \\ \operatorname{CH}_{2}=\operatorname{O}=\operatorname{CH}_{\circ} \xleftarrow{} \operatorname{CH}=\operatorname{O}_{\circ}\operatorname{CH}_{3} + \operatorname{C}_{6}\operatorname{H}_{5}\operatorname{CH}_{2} \cdot \\ \operatorname{CH}_{2}=\operatorname{O}=\operatorname{CH}_{\circ} + \operatorname{C}_{6}\operatorname{H}_{5}\operatorname{CH}_{3} \xrightarrow{} \operatorname{CH}=\operatorname{O}_{\circ}\operatorname{CH}_{2} + \operatorname{C}_{6}\operatorname{H}_{5}\operatorname{CH}_{2} \cdot \\ \operatorname{CH}_{2}=\operatorname{O}=\operatorname{CH}_{\circ} + \operatorname{C}_{6}\operatorname{H}_{5}\operatorname{CH}_{3} \xrightarrow{} \operatorname{CH}_{2}=\operatorname{O}=\operatorname{CH}_{2} + \operatorname{C}_{6}\operatorname{H}_{5}\operatorname{CH}_{2} \cdot \\ \operatorname{CH}_{2}=\operatorname{O}=\operatorname{CH}_{\circ} + \operatorname{C}_{6}\operatorname{H}_{5}\operatorname{CH}_{3} \xrightarrow{} \operatorname{CH}_{2}=\operatorname{O}=\operatorname{CH}_{2} + \operatorname{C}_{6}\operatorname{H}_{5}\operatorname{CH}_{2} \cdot \\ \operatorname{CH}_{2}=\operatorname{O}=\operatorname{CH}_{\circ} + \operatorname{C}_{6}\operatorname{H}_{5}\operatorname{CH}_{3} \xrightarrow{} \operatorname{CH}_{2} \cdot \operatorname{CH}_{2} \cdot \\ \operatorname{CH}_{2}=\operatorname{O}=\operatorname{CH}_{\circ} + \operatorname{C}_{6}\operatorname{H}_{5}\operatorname{CH}_{3} \xrightarrow{} \operatorname{CH}_{2} \cdot \\ \operatorname{CH}_{2}=\operatorname{O}=\operatorname{CH}_{\circ} + \operatorname{C}_{6}\operatorname{H}_{5}\operatorname{CH}_{3} \xrightarrow{} \operatorname{CH}_{2} \cdot \operatorname{CH}_{2} \cdot \\ \operatorname{CH}_{2} \cdot \operatorname{CH}_{2} \cdot \operatorname{CH}_{2} \cdot \operatorname{CH}_{2} \cdot \\ \operatorname{CH}_{2} \cdot \operatorname{CH}_{2} \cdot \operatorname{CH}_{2} \cdot \operatorname{CH}_{2} \cdot \operatorname{CH}_{2} \cdot \\ \operatorname{CH}_{2} \cdot \operatorname{CH}_{2} \cdot \operatorname{CH}_{2} \cdot \operatorname{CH}_{2} \cdot \operatorname{CH}_{2} \cdot \operatorname{CH}_{2} \cdot \\ \operatorname{CH}_{2} \cdot \operatorname{CH}_{2$$

$$c_{3}H_{3} \cdot + c_{6}H_{5}CH_{2} \cdot \longrightarrow c_{6}H_{5}CH_{2}C_{3}H_{3}$$

2 $c_{6}H_{5}CH_{2} \cdot \longrightarrow (c_{6}H_{5}CH_{2})_{2}$

7. The rate constant k_1 in the latter mechanism was determined from the rate of formation of methane over the temperature range 688-810°C and was given by the expression

$$k_1 = 3.6 \times 10^{13} e^{-\frac{67,000}{RT}} sec^{-1}$$
.

- 8. This activation energy was identified with $D(CH_2:C:CH-CH_3)$ and the heat of formation of the C_3H_3 radical was calculated as 73.8 kcal/mole.
- The rate constant k₂ for the homogeneous decomposition of 1,2 butadiene,

 $CH_2=C=CH-CH_3 \longrightarrow CH\equiv C-CH=CH_2 + H_2$ determined from the rate of formation of H_2 was estimated to be represented by

 $1.5 \times 10^{16} e^{-\frac{82,000}{RT}} sec^{-1}$.

- 10. It was demonstrated that the C_3H_3 radical can react as both the propargyl and allenyl radical and that it resonates between these two structures.
- 11. The propargyl structure was shown to be the favoured structure.
- 12. The C₃H₃ radical was shown to be reluctant to aostract hydrogen atoms from toluene and were removed primarily by dimerization and combination with benzyl radicals.
- 13. The average heat of formation of the C_3H_3 radical was

calculated as about 74 kcal/mole from which in conjunction with the relevant thermochemical data the following bond energies were calculated:

> $D(CH;C\cdot CH_2-H) = 81.8 \text{ kcal/mole}$ $D(CH_2:C:CH-H) = 80.2 \text{ kcal/mole}$

14. A comparison of the latter bond dissociation energies with $D(CH_3-H)$ showed that the C_3H_3 radical is stabilized by about 22 kcal/mole of resonance energy.

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