ELECTRIC DISCHARGE REACTION

OF

CARBON WITH HYDROGEN

by

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INTRODUCTION

Hydrogen, under normal conditions, is unreactive towards carbon in the chemical sense. The absence of chemical reactivity of hydrogen and carbon extends to most of the elements under normal conditions. Hydrogen and oxygen mixed in the ratio two to one respectively, can be stored, without a reaction occuring, until the mixture is exposed to a spark or a flame and under these conditions the mixture reacts with explosive violence.

The reaction of hydrogen with oxygen is generally expressed by equation (1).

$$2\ H_2 + O_2 \rightarrow 2\ H_2O \qquad (1)$$

As the equation is written, this process would require a three body collision, and some process for instantaneously breaking three bonds and forming four others. This process, although possible, is not probable from general consideration. The three body collisions as previously mentioned must occur to some extent in the gas mixture though no products are formed. The products are only formed when energy is supplied to the mixture. The energy supplied to the system must therefore create some reactive species which cause the reaction to occur. These reactive species are now firmly established to be of atomic or radical form.

HYDROGEN ATOMS

Evidence for the existence of hydrogen atoms was demonstrated by Wood, who showed that these species could be produced in a discharge tube (1).

Hydrogen atoms can be produced by several other methods, however, the basic principle of their production is the same. Hydrogen atom production depends on the ability of supplying sufficient energy to the hydrogen molecule, to increase its vibrational energy. If the energy supplied to the molecule is equal to or greater than the bond dissociation energy, then the molecule bond will break and as a result, atomic species will be formed.

The energy which must be supplied to the hydrogen molecule may originate from different sources. These sources of energy could be heat, light, electron impact, microwave, photosensitization by atoms etc..

Regardless how these hydrogen atoms are produced, they are relatively short-lived due to their reactivity either with themselves, resulting in recombination or with other atoms or radicals, resulting in compound formation. The recombination process occurs mainly on the walls of the apparatus in which they are produced. Recombination may be minimised to some extent by poisoning the walls, that is, by coating the walls with a thin layer of some chemical which does not act as a catalytic agent for the atomic recombination process. In the case of hydrogen atoms, a poisoning effect is obtained by coating the walls with orthophosphoric acid or its various sodium salts.

By minimising the recombination process, it is possible, then, to pump these hydrogen atoms from their source into another part of the apparatus where their reactions can be studied.

The reactions which the hydrogen atoms can undergo, are generally of two types;

a) Abstraction

b) Addition

To demonstrate the two types of reactions with specific examples, only the compounds containing hydrogen and carbon will be considered, as these pertain directly to the present study, though similiar processes can be extended to other systems.

Abstraction Reactions

Abstraction reactions are reactions in which a hydrogen atom abstracts another hydrogen atom from a molecule. The generalized expression is given by equation (2).

$$H + HR \longrightarrow H_2 + R \qquad (2)$$

where H is the hydrogen atom, HR is the hydrocarbon, H_2 is a hydrogen molecule, and R is a hydrocarbon with one unshared electron, termed radical.

Hydrogen Atoms With Methane

The activation energy for the reaction

$$H + CH_4 \longrightarrow H_2 + CH_3\cdot \qquad (3)$$

has been controversial for many years, however, reaction (3) was thought to be the primary step (2).

In 1937, Steacie (3) investigated this reaction using deuterium atoms, and although the exact mechanism of the reaction was undecided, he concluded that the initial step was an abstraction reaction

$$D + CH_4 \longrightarrow CH_3\cdot + HD \qquad (4)$$

In 1953, Berlie and Le Roy (4) indicated that an abstraction reaction is probably correct.

In 1964, Jamieson and Brown (5) reported ethane as their product from a reaction of hydrogen atoms (generated in an electric discharge) with methane above 500° C. The amount of methane reacted under these conditions, approached very closely the amount of hydrogen atoms capable of reacting. The amount of ethane formed was half of the amount of methane reacted indicating that reaction (3) probably occured to give CH_3 species, which participated in ethane formation.

Hydrogen Atoms With Ethane

As with methane, the controversy over the hydrogen atom ethane reaction lasted for several years (2). Steacie and Phillips (6) from their study of deuterium atoms with ethane, suggested reaction (5) to take place.

$$D + C_2H_6 \longrightarrow C_2H_5 + HD \qquad (5)$$

Berlie and Le Roy (7) concluded from their investigation of H atoms, produced by a hot filament, with ethane that reaction (5) does occur. The reaction of hydrogen atoms with propane has also been investigated (8). The results from this study indicated that the abstraction reaction is also operative. From these and other studies, it is indicative that the abstraction may occur with any hydrocarbon which has an abstractable hydrogen.

Addition Reaction

Hydrogen atoms react with unsaturated hydrocarbons by the addition to the double bond. This reaction can be shown by the following equation:

$$R{=}R + H \longrightarrow \overset{H}{\overset{\backslash}{R}} - R. \qquad (6)$$

The radical produced in reaction (6), is itself very reactive, and can undergo further reactions. The reactions of radicals will be discussed later in the thesis.

Specific examples of hydrocarbons which undergo hydrogen atom addition reaction are ethylene and acetylene.

Hydrogen Atoms With Ethylene

The reaction of hydrogen atoms with ethylene gives ethyl radicals as the intermediate radical product;

$$H + C_2H_4 \longrightarrow C_2H_5. \qquad (7)$$

Reaction (7) was first investigated by Von Waternburg, and Schultze (9), whose results indicated the process as given in reaction (7) to occur. Other workers (2) (10) (11) verified that addition to double bonds does occur.

Hydrogen Atoms With Acetylene

The reaction of hydrogen atoms with acetylene, in the early stages of investigation, appeared to be non-existent. It was shown by Geib and Steacie (2), in their study of deuterium atoms with acetylene, that a reaction did occur, as they obtained as their reaction products deuterated acetylene. From their results they suggested the following mechanism which would explain why no reaction was observed by other workers using hydrogen atoms.

$$C_2H_2 + D \longrightarrow C_2H + HD \qquad (8)$$

$$C_2H + D \longrightarrow C_2HD \qquad (9)$$

$$C_2H_2 + D \longrightarrow C_2H_2D \qquad (10)$$

$$C_2H_2D + D \longrightarrow C_2HD + HD \qquad (11)$$

Le Roy and Steacie (12), studied the reaction of hydrogen atoms at low and high concentration with acetylene, and have shown that at low hydrogen atom concentration ethylene was formed. From their results they concluded that the formation of the vinyl radical (C_2H_3) is a necessary step before further hydrogenation can take place to give ethylene as a product.

Hydrogen Atoms With Carbon

The reaction of hydrogen atoms with elemental carbon, in a form of soot, was shown to occur at 100° C. from independent studies by Avramenko (13) and Harris and Tickner (14). Avramenko reported that the reaction showed an emission band at 4317 A° indicating C-H radicals to be present. The report of Harris and Tickner indicated that hydrocarbons were actually formed and methane was the chief product with small amounts of C_2 to C_5 hydrocarbons.

More recent studies of hydrogen atoms with carbon, indicated that the C_2 species were generally ethane and ethylene(15,16).

Shahin (15) in his work on hydrogen atom reaction (produced by microwave discharge) with solid graphite reported acetylene to be present among his products. King and Wise (16) reported acetylene to be only important as a product at higher temperatures, although hydrocarbons up to C_7 were observed by these investigators.

ATOMIC CARBON

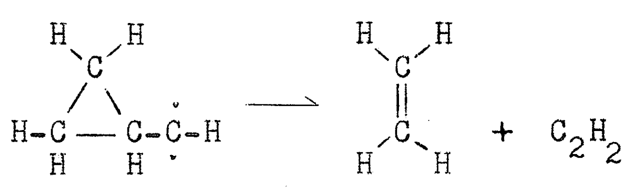
The reaction of atomic carbon (produced by a nuclear process) was studied with several hydrocarbons. McKay and Wolfgang (17) reacted atomic carbon with methane, ethane, propane, cyclopropane, and propylene. The reaction products from these hydrocarbons showed that acetylene was the major constituent, and ethylene was generally secondary in abundance. The authors were able to explain their high yields of acetylene on assumption that the carbon atom inserted into the C-H bond of the hydrocarbon. The generalized form for this reaction, as given by the authors, is;

$$R\text{-}\overset{R''}{\underset{H}{C}}\text{-}H + \dot{\underset{\cdot}{C}}\colon \longrightarrow R\text{-}\overset{R''}{\underset{H}{C}}\text{-}\dot{\underset{\cdot}{C}}\text{-}H \qquad (12)$$

The carbene (the product from reaction (12)), thus formed, may be collisionally de-excited to a singlet state (as the atomic carbon is assumed to react in the triplet state), causing decomposition by the following process;

$$R\text{-}\overset{R''}{\underset{H}{C}}\text{-}\ddot{C}\text{-}H \longrightarrow R\text{-}R'' + C_2H_2 \qquad (13)$$

It is also possible, as the authors have suggested, that the process may involve a direct rupture of two C-C bonds, if sufficient energy is available, by the insertion process. The carbene formation can only arise from carbon insertion into the hydrocarbon C-H bond. In the case where the hydrocarbon is cyclopropane, the carbene formed should favor acetylene formation, as simple electronic rearrangement can form stable products, as is shown by the reaction;



(14)

In confirmation to this process, the amount of acetylene formed from this reaction was found to be approximately twice the quantity obtained from the reaction with other hydrocarbons.

The reaction of carbon atoms with propane yield ethylene, propylene, allene, methylacetylene, and butadiene. The small yields of butene-1 and isobutene from this reaction, as explained by the authors, arose from the deactivation of the intermediate carbene without decomposition. The carbon atom can insert into propane in two different positions as is shown by the following equation;

```
.      H H H           . H H H
C  +  H-C-C-C-H  --->  H-C-C-C-C-H          (15)
.      H H H           . H H H
```

or

```
                          H
                         ·C·
.      H H H            H | H
C  +  H-C-C-C-H  --->  H-C-C-C-H            (16)
.      H H H            H H H
```

Deactivation of the intermediate carbene from equation (15) would form butene-1. Similiarly deactivation of the intermediate carbene from equation (16) could form isobutene.