Introduction

With the rapid development of electrical power generation from nuclear energy, and the virtually certain advent of fusion reactors, the future for electrical energy seems to be one of relative continuing cost constancy. Where does this leave the chemical industry? We see desirability in directives of this electrical energy source,

Chemical Reactions in a Silent Electric Discharge

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concomitant conservation of fossil organics for raw materials. In this article we discuss the use of silent electric discharge as a means of getting energy into chemical reactions. The basic principle behind this process is getting activation energy directly from hot electrons.
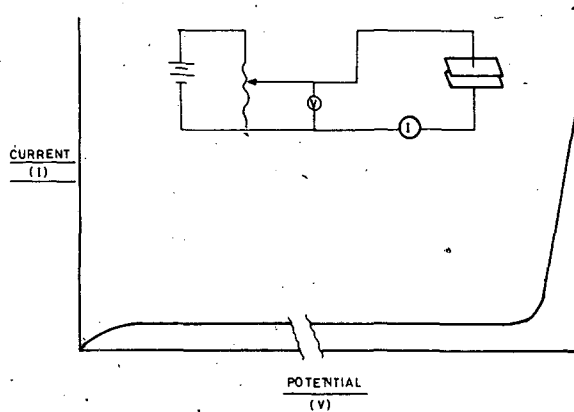
Electrical characteristics

Fig.1: The voltage-current relationship that prevails in a simple parallel plate discharge device.

Fig. 1 illustrates the voltage-current relationship that prevails in a simple parallel plate discharge device. At low voltages, as the voltage rises, the current rises too. This small current is said to be due to ionising radiations forming ion pairs between the electrodes. These ion pairs drift to the charged plates and account for the observed current. Eventually, the current levels off because natural radiation provides only a limited number of ions per second. Continued increase in the voltage and field strength carry the system into another region, the CORONA region. A corona is characterised by a low current electrical discharge, across a gas filled gap at a voltage gradient on the order of the sparking (electrical breakdown) potential of the gap. During the breakdown, the gas becomes partially ionised and a characteristic, diffused, bluish glow results. Kilovolt voltages and milliampere to ampere currents are typical within a corona. On the opposite end of the spectrum, an arc discharge is characterised by a high current density causing a highly ionised gas and a low voltage gradient in the gap.

Here some molecules of the surrounding gas have thermal energies such that when they hit a charged electrode they can gain or lose charge forming gaseous ions and provide for additional current capacity in the gas. Now, only a small increase in the field strength can accelerate the corona ions to energies high enough to create more ions as they collide with gas molecules. The resulting avalanche , as it is called, makes available virtually unlimited charge carriers and the current rises to values limited only by the physical materials themselves.

An electrical insulator is placed over one or both electrodes. An outer tube and a liquid electrode (water) in the inner tube form the electrodes across which is applied an electric field. Gaseous reactants are passed through the electric field in the annular space between the tubes, and products are recovered on an appropriate collection system downstream. Generally,

the electric source is a ballasted neon sign-transformer rated at 15 KV (rms) at 30 mA, with 120 volts, 60 cps in the primary. In order to study power consumption the source is varied from the regular 60 cycles sinusoidal wave to the other types of fields such as pulsed, square waves, etc.

Chemical reactions

(SUPPORTED BY EXPERIMENTAL EVIDENCE)
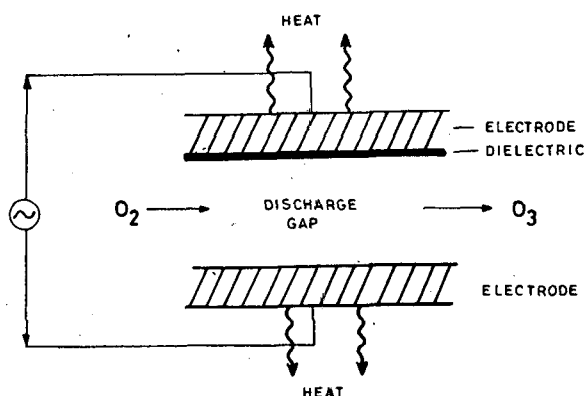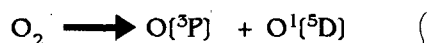

Fig.2: A typical corona cell.

When oxygen is passed through a reactor, like the one illustrated in Fig.2, it undergoes decomposition into two atoms.

$$O_2 \longrightarrow O(^3P) + O^1(^5D) \quad ($$

The atom in the ^{3} P (ground) state can readily react with molecular oxygen in the presence of a third body to form ozone.
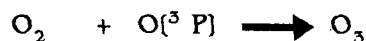
$$O_2 + O(^3 P) \longrightarrow O_3$$

Fig. 2 depicts a typical corona cell consisting of two metallic electrodes separated by a gas filled gap and a dielectric material. A reactant bearing a gas flows through the discharged gap while high voltage is applied to the electrodes. Most of the electrical energy input to the corona is dissipated primarily as heat with smaller portions going to light, sound and chemical reactions.

Electrically, a corona cell presents a capacitive load to the power supply due to both the gas filled gap and the dielectric materials present. Products are formed in the corona as a direct result of power dissipation in the corona.

Apparatus

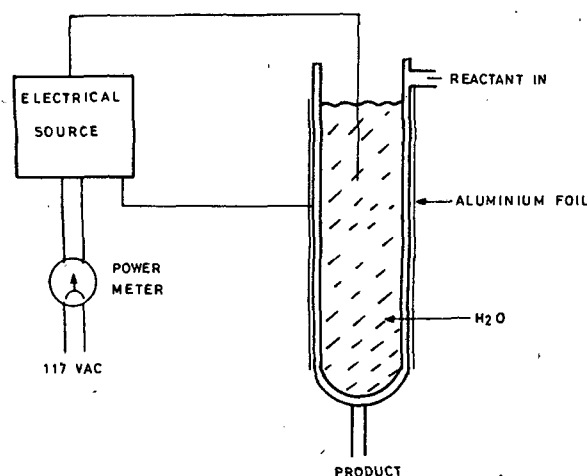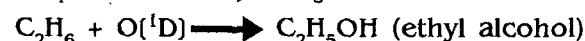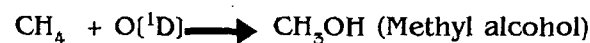The apparatus used in this studies is in general identical to a standard ozone generator.

Fig.3: A schematic representation of the reactor.

Fig.3 is a schematic representation of the reactor, which consists of two concentric glass tubes. A layer of Al foil rapped around the $O^1($ D) is left with nothing to react and a forbiddentransition to the ground state ^{3} P . Warneck estimates the half life of $O^1($ D) at around 100 seconds under certain conditions. Experiments in this work confirm the relatively long life time of atomic oxygen, though no attempt has been made to measure it.

Silent electric discharge thus finds its best application in the synthesis of ozone. · Also, when oxygen was passed through the reactor and mixed with methane after passing out of the field, methanol was detected as a reaction product. It is significant that it was the only product detected.

Thus $O^1($ D) is reactive with molecules such as methane, ethane, benzene and olefins.

$$CH_4 + O(^1D) \longrightarrow CH_3OH \text{ (Methyl alcohol)}$$
$$C_2H_6 + O(^1D) \longrightarrow C_2H_5OH \text{ (ethyl alcohol)}$$
$$C_3H_6 + O(^1D) \longrightarrow H_2C\text{-}CH_2 \text{ (epoxide)}$$
$$\backslash \, /$$
$$O$$

$$C_6H_6 + O(^1D) \longrightarrow C_6H_5OH \text{ (phenol)}$$

Carbon dioxide seems to be a good

candidate for study in a silent electric discharge as it is known to decompose to CO and O_2

One mechanism that has been proposed is:

$$CO_2 \xrightarrow{\text{(e)}} CO + O$$
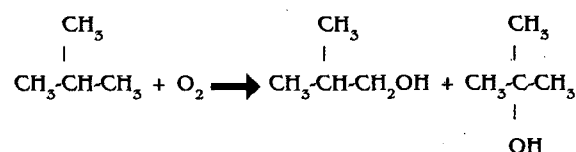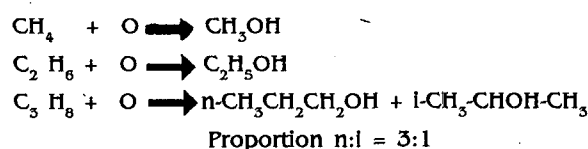
$$O + CO_2 \longrightarrow O_2 + CO$$
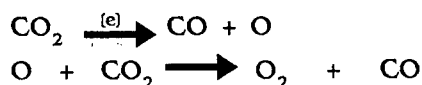
When mixtures of CO_2 and paraffins were passed through the reactor, the predominant reactions of the O atoms were characteristic of the singlet state.

$$CH_4 + O \longrightarrow CH_3OH$$

$$C_2H_6 + O \longrightarrow C_2H_5OH$$

$$C_3H_8 + O \longrightarrow n\text{-}CH_3CH_2CH_2OH + 1\text{-}CH_3\text{-}CHOH\text{-}CH_3$$

Proportion n:l = 3:1

$$\underset{\overset{|}{CH_3}}{CH_3}\text{-}CH\text{-}CH_3 + O_2 \longrightarrow \underset{\overset{|}{CH_3}}{CH_3}\text{-}CH\text{-}CH_2OH + \underset{\overset{|}{OH}}{CH_3}\text{-}C\text{-}CH_3$$

The readers may think that the insertion in the C-H bond is random as strongly suggested by the reaction with propane and i-butane. But these reactions are relatively clean.

There is some free radical chemistry, owing to O(^{3} P) atoms but these are probably less than 10% of the O atoms reacting. The hydrocarbons give minor amounts of olefins, acetylene, etc. when passed through the reactor without oxygen, so some secondary products show up.

The CO fragment from the decomposition of CO_2 seems to be formed in an excited state, but it must drop rapidly into its ground state. Reaction products attributed are :

$$CO + CH_4 \longrightarrow CH_3\text{-}CHO$$

$$CO + C_2H_6 \longrightarrow CH_3\text{-}\overset{\overset{O}{\|}}{C}\text{-}CH_3 + CH_3CH_2CHO$$
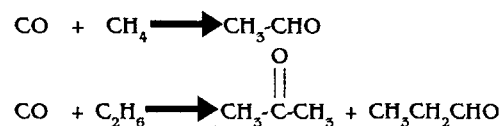
The formation of acetone is rather surprising. No mechanism is implied by writing their reactions and the pathway is rather complex. Reactions of CO_2 with olefins are still dominated by the role of O atom as in the case of paraffins. Here again, the products are typical of the singlet state O atoms.

$$C_2H_4 + O \longrightarrow \underset{O}{H_2C\text{-}CH_2}$$

$$CH_3\text{-}CH=CH_2 + O \longrightarrow \underset{O}{CH_3\text{-}HC\text{-}CH_2}$$
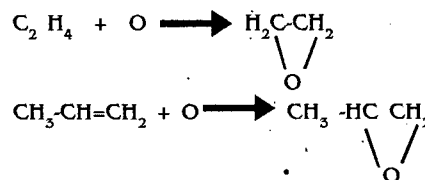
In the case of olefins, polymerisation of the parent olefins complicates the product spectrum.

If olefin alone is passed through the reactor it polymerizes.

$$C_2H_4 \xrightarrow{\text{(e)}} (C_2H_4)_n \qquad n = 2,3,4, \text{ etc.}$$
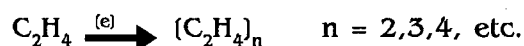
The olefin products formed are C_4 through C_8 : the C_4 predominates. The higher olefins are mostly alpha olefins, but hydrogenation to paraffins occurs to some extent. The typical analysis of the C_6 olefin group shows the following types :

1. $R\text{-}CH=CH_2$ 57%
2. $(trans)R_1\text{-}CH=CH\text{-}R_2$ 22%
3. $(cis)R_1CH=CH\text{-}R_2$ 6%
4. $R_1R_2C=CH_2$ 15%

This product mixture indicates that the initiating species is probably an excited electronic state for ethylene and the energies involved lead to extensive rearrangements. Propylene does not easily polymerize beyond the dimer. More than 90% of the product formed when propylene is passed through the reactor can be accounted for in the following distribution.

2-methylpentene	46.5%
4-methyl-1-pentene	24.3%
4-methyl-2-pentene	1.3 %
2,3-dimethyl-1-butene	2 %
2-methyl-1-pentene	2.1 %
hexadienes	18 %
hexynes	4.9 %
2-hexene-4-yne types	0.9 %

These structural types are of interest as raw materials for isopropene. Most have the skeleton structure of 2-methylpent-2-ene which is pyrolysed to isopropene commercially.

$$CH_3$$
$$|$$
$$C=CH\text{-}CH_2CH_3 \xrightarrow{\text{heat}} CH_2=CH\text{-}CH=CH_2 + CH_4$$
$$|$$
$$CH_3$$
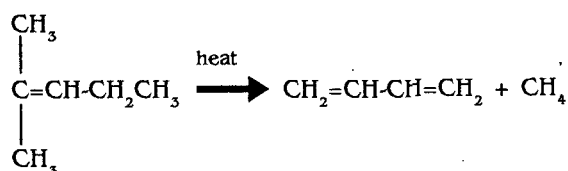
The most interesting chemistry is observed in the reactions of ammonia. Ammonia adds to the double bond of olefins quite clearly. The only complicating factor of significance seems to be the formation of higher olefins, with subsequent addition of ammonia.

| Reactions of olefins and ammonia		Yield
$C_2H_4 + NH_3 \longrightarrow C_2H_5NH_2$		60%
$C_3H_6 + NH_3 \longrightarrow$ n-$C_3H_7NH_2$		8%
	i-$C_3H_7NH_2$	36%
	allyl amine	24%
	C_6 amines	32%
$C_6H_{10} + NH_3 \longrightarrow C_6H_{11}\text{-}NH_2$		
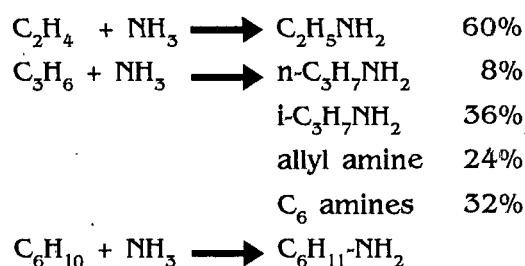
The formation of substantial amounts of allyl amine with propylene leads to speculation about the attacking species. It is conceivable that the initial reaction of ammonia is the formation of nitrene .

$$NH_3 \xrightarrow{(e)} NH + H_2 \cdot$$

followed by the attack of the olefins.

$$NH + C_3H_6 \longrightarrow C_3H_5NH_2$$

Since there is plenty of hydrogen available from ammonia decomposition, the saturated n- and i-propyl amine could be the secondary products. A very surprising product, methyl pyridine is obtained.

$$C_6H_6 + NH_3 \longrightarrow \text{methyl pyridine}$$
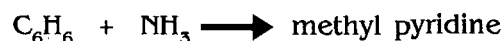
Ferolinsky, Feyer and others have shown that certain nitrenes react with benzene to give seven membered heterocycles.

They showed that the nature of the products and the reactivity of nitrene is dependant on alkyl group attached to the ring. It is possible that such intermediates could form the methyl pyridine observed. In the reaction of olefins such as ethylene, propylene with ammonia, the products include the dimers and polymers normally observed when olefin alone is passed through the reactor. These products must arise from the electronic excitation of the olefin directly. In the presence of ammonia, the active olefin could react with molecular ammonia to give the saturated amines. Further work on the mechanisms of these reactions with ammonia seems to be very much in order.

The reaction of ammonia and acetylene to give a product analogous to vinyl amine or ethylene amine was attempted. The product was not completely chracterised, but appeared to be a complex mixture of polymeric products of acetylene containing both amino and nitrile groups. Acetylene alone gives an intractable in the discharge reactor. The polymer formed in the presence of ammonia is of lower molecular weight and is soluble in a variety of solvents, owing largely to the presence of nitrogen. About half of the liquid products consist of ethyl amine and probably come from the reaction of ammonia with ethylene, which in turn is formed by acetylene hydrogenation.

Conclusion

Plans for future work call for a continued effort in improving power yields, reactor designs, chemical yields and conversions for reactions of chemical interests.

References

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