PLASMA EXTINCTION BY FLAME INHIBITORS

by

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Participating in
Junior Scientist and Engineer
Program
1960

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ABSTRACT

For a few compounds on which data are available, there is a parallel between the ability of the compound to capture and more-or-less permanently remove electrons from a flame and its efficiency as an extinguishing agent. Because a gaseous discharge plasma is a much simpler system than a flame, a preliminary study was made of the ability of fire extinguishing agents to extinguish a low pressure discharge in argon.
1. INTRODUCTION

Many compounds used in the inhibition of flames have been shown to have rather large cross-sections for dissociative electron attachment, that is, processes such as \( \text{CH}_3\text{Br} + e^- \rightarrow \text{CH}_3 + \text{Br}^- \). Papers by Dibeler, Reese, and Mohler \(^1,2\) give data indicating the relative abundance of the negative ion formed. These abundances, measured by means of a mass spectrograph, must give an indication of the ability of the neutral gas molecules to attach electrons.

If a list of various compounds on which attachment data are available is formed in decreasing order of negative ion abundance, it is found that the list is identical, entry for entry, to the list formed by ordering the same compounds in decreasing effectiveness as extinguishing agents. There is no apparent correlation between the actual magnitudes on both lists, but the coincidence in crude ordering is enough to motivate more detailed study of the role of electron attachment in flame inhibition.

2. FLAME INHIBITION

The effectiveness of many gaseous compounds in flame extinguishment has been found empirically in experiments done for the Army Engineers Research and Development Laboratories \(^3\). These experiments measured, for many gaseous compounds, the maximum percentage (by volume) necessary to extinguish a flame composed of variable amounts of n-heptane and air. The fuel, air, and inhibitor were mixed together in a combustion tube containing a spark gap. The mixture was considered flammable if, when a high voltage was applied, ignition occurred and the flame front propagated to the end of the combustion tube.

There are three important things to note along with the data given in the report. 1) "The relative flame inhibiting effectiveness of any of the agents investigated does not vary appreciably with variation in the type of fuel (hydrocarbon or oxyhydrocarbon), or of the temperature of the atmosphere in which the flame is propagated." 2) Most of the data were taken at pressures of 400-500 mm Hg. "Little variation in the flammable limits was observed with changes in pressure from about 200 mm Hg. to atmospheric pressures." 3) Concerning temperature dependence, tests were made at -78C, 27C, and 145C. It was found that although the percentage (for extinguishment) of a given inhibitor changed, the ratio between any two gases did not vary appreciably.
3. PROPOSAL

A flame, which is a mixture of free electrons, neutral air and fuel molecules, free radicals, and many varieties of ions, may be considered to be a very complicated type of plasma. Its complexity is several magnitudes higher than that of a gas discharge in one species, for example, an inert gas. It is made more complex not only because of the different species present, but because of the chemical reactions between different ions which are usually not inert. Free radicals are present also, along with the chains of free radical reactions used to explain flame propagation.

To avoid some of these complications, it was decided to determine the effect of flame inhibitors on the parameters of an argon plasma. These parameters, such as voltage, current, and pressure, have the advantage of being simple and easily measurable.

4. EQUIPMENT

A gas discharge tube was constructed from the design given in figure 1. It was necessary to have platinum electrodes (made from .004" platinum foil) to prevent corrosive action by some of the inhibitor gases. It was also desirable to make one electrode movable to give more variation in the values of electric field strength between the electrodes. A schematic of the electrical circuitry used is given in figure 2a. Details of the gas flow system are given in figure 2b. To facilitate the changing of the inhibitor to argon ratio, a dynamic system was used, with flowmeters selecting the desired amounts of gases. Most of the mixture was bubbled through water into the atmosphere; only a small portion was bled off and sent to the discharge tube. The vacuum pump operated continuously and maintained a constant pressure in the tube.

5. EXPERIMENTAL PROCEDURE

The discharge tube was evacuated to the limit of the mechanical pump (about 200 microns), filled to atmospheric pressure with Argon, and evacuated again. This process was repeated for several hours. Following this, argon alone was pumped continuously through the system for one day. The pressure remained at about 1 mm Hg.

Because an oil diffusion pump was not available, the pressure could not be lowered below a few hundred microns. This means that there was still a rather large concentration of impurities remaining both as free gases and substances on the walls of the tube. For this reason (and convenience in obtaining gases) no special effort was made to use ultra-pure gases or extremely "clean" procedure. This necessarily made the experiment somewhat crude but since it was preliminary work, extreme accuracy was not required.
With the pressure at 1 mm, the electrodes spaced 1.5 cm apart, a discharge was generated in argon. Under normal conditions the voltage was about 250 volts, the discharge current, from 30-60 ma. The discharge exhibited the normal characteristics of a glow discharge, such as dark spaces and striations. Variable amounts of the inhibitor gas were then fed into the tube.

In the first experiment, the discharge current was plotted as a function of the percentage (by volume) of the inhibitor gas. This was an attempt to see if the inhibitor would extinguish the discharge, regardless of the voltage fluctuations across the tube (due to the changing discharge current). Because of the resistor in series with the tube, there were two competing effects present. The constraint, of course, was that the total voltage across the resistor and the tube must remain constant (the constant output voltage of the power supply). Now, as the inhibitor gas was introduced, the discharge current (hence, the total current in the circuit) dropped. This decreased the voltage across the resistor and therefore, increased the voltage across the discharge tube. This "feedback" voltage increased the amount of ionization and tended to oppose the drop in current caused by the inhibitor. The net effect is shown in figure 3. As the voltage across the tube increased, the glow region was constricted to a very bright narrow beam between the electrodes. At 25% inhibitor, the discharge current had dropped to less than 10 ma. The current flow, however, was constricted to such a small area, that the plates were overheating. At this point, the experiment was discontinued, the only conclusion being that the introduction of the inhibitor gas caused an immediate drop in discharge current.

In the second experiment, the voltage across the discharge tube was held constant, regardless of the current flow. This, of course, is necessary to maintain a constant average electron energy. With the introduction of approximately .5% CF$_3$Br, the discharge current dropped, the voltage started rising and on being manually returned to the initial value, the discharge was extinguished. After changing the flowmeters so that a smaller amount of inhibitor could be admitted, the experiment was again attempted. This time, the discharge current remained constant (within 1 or 2 ma) until .11% CF$_3$Br was reached. The voltage started to rise but was held constant by lowering the supply output voltage. This caused the current to drop about 10 ma from the initial value. Apparently, at this point, an equilibrium state existed. As long as the percentage of inhibitor was not changed, the voltage and current remained the same. With the slightest increase of inhibitor, however (to somewhat less than .12%), the discharge was extinguished.
On each attempt, it was found that the extinction point was reached very abruptly. The discharge current remained constant until a certain concentration was reached or a rate of production exceeded. The current was then driven to zero.

The amount of inhibitor is very small, being slightly more than one molecule of inhibitor per thousand molecules argon. This ratio is considerably smaller than that required to extinguish a flame of n-heptane. CF$_3$Br, for example, is 50 times more effective in plasma extinction than in flame.

The same experiment was then tried with two other inhibitor gases, CF$_3$Br and CCl$_2$F$_2$. In each case, the same sharp cutoff was reached. The current as a function of percent inhibitor curves for three gases is shown in figure 4.

Above, it was mentioned that the effectiveness of the inhibitors in plasma was much higher than in flame. The connection between these observations is not obvious. It is, however, interesting and important to compare the ratio of the effectiveness of any two given inhibitors in plasma with the ratio of the same two gases in flame extinction. This information for three gases is given below.

<table>
<thead>
<tr>
<th>Inhibitor gas</th>
<th>Amount by Vol. to extinguish flame</th>
<th>Ratio</th>
<th>Amount to extinguish Plasma</th>
<th>Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>CF$_3$Br</td>
<td>6.1%</td>
<td>.63</td>
<td>.120</td>
<td>.676</td>
</tr>
<tr>
<td>CH$_3$Br</td>
<td>9.7%</td>
<td>.63</td>
<td>.178</td>
<td>.676</td>
</tr>
<tr>
<td>CH$_3$Br</td>
<td>9.7%</td>
<td>.65</td>
<td>.178</td>
<td>.675</td>
</tr>
<tr>
<td>CCl$_2$F$_2$</td>
<td>14.9%</td>
<td>.65</td>
<td>.264</td>
<td>.675</td>
</tr>
</tbody>
</table>

The agreement of the ratios is quite close, which is all the more unusual considering the crudeness of the data.

Incidentally, a fourth inhibitor gas (CHClF$_2$) was attempted. Only a crude idea of the extinction percentage was found though. It was in the proper order with respect to the three inhibitors mentioned above. Before the percentage was measured accurately, water was accidentally fed into the discharge tube. Time did not permit making any more measurements after cleaning the tube.
6. DISCUSSION

Assuming now that the ratios are the same, as the evidence indicates, the following conclusions may be drawn. Since the effectiveness of any inhibitor bears the same fixed relation to those of the other inhibitors, in both flame and plasma, it is implied that the mechanism for extinction is the same in both flame and plasma. The increased efficiency of an inhibitor in a plasma then must be attributed to a larger amount (or higher collision rate) of some vital constituent, for instance, more electrons per inhibitor molecule. This, however, is not yet clear.

One thing of importance follows almost immediately. Inhibition does not occur by interruption of free radical chains which have been proposed to explain flame propagation. This is true since the extinction mechanism is indicated to be the same in both plasma and flame and there are no free radical chain-type reactions in plasmas.

It has also been suggested that inhibition occurs by interrupting some form of energy feedback. In flames, this feedback energy is directed to the reacting gases. The energy could be either radiant or thermal in nature. It is probable that neither of these forms is important in a plasma, which receives energy continuously from the voltage source connected across the electrodes. No feedback energy, then, is necessary to maintain the glow discharge. As a point of interest, certain halogenated hydrocarbons, similar in nature to the inhibitors used here, have been used as "quenching agents" in Geiger counter tubes. Supposedly, their purpose is to absorb infrared radiation in the tubes to prevent secondary signals. Evidently these compounds have wide absorption bands in the infrared region. Some information on this is available in Brown's "Basic Data of Plasma Physics". If we rule out radiant energy feedback in a plasma, interruption of this chain as a mechanism for inhibition must be discounted as a consequence.

It seems clear also that the mechanism is not one of simple dilution. An experiment which should have been performed is the introduction of a "dummy" gas, inert in nature, during the discharge. Since argon has such a high ionization potential, the actual discharge should be carried out in another inert gas, with argon used as the "dummy inhibitor". This would verify that dilution is not important.

It is important to note the loss or decay mechanisms in a plasma. Calcote /4/ mentions the three principal mechanisms; ion recombination, diffusion to the walls with recombination, and electron temperature decay. To these, in relevant situations, he adds charge exchange and electron attachment. Now, the inhibition mechanism must be connected in some manner, with at least one of these mechanisms. In view of the mass spectrographic data showing the high cross-sections for electron attachment of the
inhibitors, it would be very tempting to state that electron attachment is the sole mechanism. However, there will be interaction between these modes of decay. Calcote says, "...when electro-negative gases are present, electron attachment will greatly affect the rate of ion recombination and will greatly reduce the ambipolar diffusion coefficient." These other side effects, as opposed to attachment which is most likely the major loss, may account for the large difference in efficiency of an inhibitor in plasmas and flames; the latter having a much greater variety of ions, neutrals and free radical.

7. SUMMARY

1. The inhibition mechanism used by the gases that were tested appears to be the same in both plasma and flame.

2. Since there are no free radical reactions in a simple plasma, inhibition does not occur through interruption of free radical chains.

3. Inhibition does not operate through simple dilution.

4. In view of the limited number of loss mechanisms in a plasma, all dealing with electrons, inhibition must occur through direct loss of electrons through attachment and/or modification of the other loss mechanisms as rate of ion recombination and ambipolar diffusion.

8. SUGGESTED MODIFICATIONS IN EQUIPMENT

1. A discharge tube with permanent electrodes spaced about 1.5 cm apart should be constructed. The plates should be smaller in diameter (about .5 or .75 inches in diameter) and the glass envelope, much larger (2 inches in diameter) to prevent heating of the glass near the rim of the plate.

2. Three inlets should be provided, a vacuum indicator, a lead to the vacuum pump, and a lead to the entering gases. Both of the latter should be provided with double stop cocks.

3. A high vacuum system should be used consisting of a roughing pump, oil diffusion pump and liquid N₂ cold trap.
9. SUGGESTED EXPERIMENTS

1. All experiments listed previously should be repeated with as many additional inhibitors as possible.

2. The experiment should be repeated using several "dummy" inhibitors such as other inert gases.

3. All of the experiments above should be run in various inert gases in place of argon. The average electron energy in each gas will be different. This should produce somewhat different efficiency ratios since the capture cross-section of each inhibitor will vary differently with energy.
10. REFERENCES

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Northwestern University, Evanston, Ill., Aug. 24-26, 1959.
Fig. 2a. Electric Circuit

Fig. 2b. Gas Flow System
FIG. 3 - DISCHARGE CURRENT VS PERCENT INHIBITOR
FIG. 4 - DISCHARGE CURRENT VS PERCENT INHIBITOR
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