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FLAME INHIBITION WITH ELECTRON ATTACHMENT AS THE FIRST STEP

by

Robert M. Mills

NBS

U.S. DEPARTMENT OF COMMERCE
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ABSTRACT

The suggestion is made that combustion inhibition of the type observed with the use of most halogenated hydrocarbons is due to a two-step process: (1) negative ions and free radicals are formed by dissociative electron attachment with the inhibitor molecules, and then (2) these negative ions and/or free radicals react with the free radicals found in flames. Considerable evidence from the literature is presented which supports this idea. It is concluded that, while the evidence is not conclusive, a serious consideration of the idea is justified.

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1. Introduction

There is considerable evidence to show that nitrogen and carbon dioxide are effective as fire suppressants primarily through their action as diluents and cooling agents. For some time, however, it has been recognized that other agents are considerably more effective in inhibiting combustion reactions. Many of the halogenated hydrocarbon compounds are of this type. In spite of their high heat capacity, they do not, when applied in less than extinguishing concentration, lower flame temperatures appreciably, suggesting that another more effective mechanism is at work.

The inhibition mechanism currently receiving the most attention starts with the observation that large concentrations of H, OH, and O free radicals are generated in the reaction zone of a flame. These free radicals are thought to be essential in the perpetuation of the flame. Inhibition is attributed to flame free radicals reacting in some way with the inhibitor, making H, OH, and/or O unavailable for the combustion process. Numerous authors have discussed this theory [1-5]. Spectroscopically, OH absorption lines have been observed to decrease as $Fe(CO)_5$, one of the best inhibitors known, is added to a hydrocarbon flame [6]. Recently, Zeegers and Alkemade [7] studied recombination reactions of excess flame radicals and concluded that H, OH, and O concentrations are related to one another. That is, a depletion of one free radical species would also cause a reduction in the concentration of the others. If this is true, it should not be important which flame radical reacts with the inhibitor.

The free radical depletion theory fails to provide a clear explanation for the observation by Creitz [8] and Lee [9] that there is a correlation between electron attachment cross section and inhibitor effectiveness. Good inhibitors also have large electron attachment cross sections. The observed facts may be combined by proposing an electron attachment process as the first step in an inhibition mechanism, the step that generates active species which then react with the flame free radicals. This paper examined such a possibility. Most of the evidence presented was obtained from the literature.

2. Proposed Inhibition Mechanism

A typical flame inhibitor, CF_3Br_1, attaches low energy free electrons by the dissociative attachment process [10] [11]:

$$CF_3Br + e^- \rightarrow Br^- + CF_3 \tag{1}$$

The negative ions and free radicals which result are very reactive. Inhibition could take place through the reaction of O,OH, and/or H (or possibly other molecular fragments from the fuel) with the negative ion and/or the radical which remains after the negative ion detaches from the parent inhibitor molecule. This radical will hereafter be referred to as the residual radical.

Consider first the possibility that inhibition is due to the reaction between the residual radical and free flame radicals. Using the inhibitor mentioned above, H, for example, could be removed as follows:

$$CF_3 + H \rightarrow CF_3H^* \tag{2}$$

The resulting molecule from this reaction is formed with excess energy equal to the heat of formation. The excess energy would be lost by collision with a third body, M:

$$CF_3H^* + M \rightarrow CF_3H + M^* \tag{3}$$

Several other authors have mentioned the ability of these residual radicals to inhibit, although their comments were not associated with electron attachment. Rosser, Wise, and Miller [12] proposed in the Seventh Combustion Symposium that "the effectiveness of bromine-containing inhibitors is essentially equal to that of an equivalent amount of bromine" in methane-air mixtures of maximum flame speed. Then, in comparing the effectiveness of CF_3Br and 1/2 Br_2, they concluded that the CF_3 radical must contribute to the inhibition process. Fenimore and Jones [3] presented evidence which "suggests that methyl radicals from either methane or methyl bromide are powerful inhibitors" in CH_4-H_2- air mixtures. They suggest that methyl radicals react mostly with oxygen atoms in air or O_2 flames [33], making the oxygen radical unavailable for the normal combustion reaction.

Return now to the possibility that the negative ion formed in the electron attachment process is the important agent in removing flame free radicals. For example, H could be removed by:

$$H + Br^- \rightarrow HBr + e^- \tag{4}$$

In this case, a stabilizing reaction similar to (3) is not necessary since the excess energy can be carried away by the electron.

Regardless of whether the residual radicals or negative ions are the important agents, the overall result is the same as in the inhibition theories mentioned in [1-5], i.e., there is a reduction in concentration of active free radicals in the inhibited flame. The uniqueness of the mechanism proposed here is reaction (1). Electron attachment may be necessary to supply the residual radicals and/or negative ions which then react with the flame radicals, thereby explaining the electron attachment correlation.

3. Supporting Observations

3.1 Electron Attachment in Inhibited Flame

One of the first questions which arises when examining the validity of the proposed inhibition mechanism is whether negative ions are found in a flame when inhibitors are added. Several experimenters report that they are. Feugier and Van Tiggelen [15] observe that Cl^- ions appeared with addition of the slightest trace of chlorine compounds. Calcote et al [16] reports Cl^- resulting from addition of PCl_3, and Miller observed [14] that negative ions can be detected when CCl_4 is added to a flame.

In order to further substantiate the idea that inhibitors are good electron attachers and to study the type of attachment taking place, a qualitative study was made in this laboratory of the predominant negative ions formed from (each) of 20 compounds in an electron bombardment ion source using a time-of-flight mass spectrometer [11]. Most, but not all, of the compounds studied are considered to be good flame inhibitors. The energies of the bombarding electrons in the source were distributed roughly over the same range as those believed to exist in flames, i.e., 0 to 1 electron volts. Table I summarizes the results. Without exception, all effective inhibitors formed negative ions by the dissociative attachment process. Most of the halogenated inhibitors detached one of the halogen atoms.

Malcolm rates SF_6 as only slightly more effective than CO_2 [20]. Yet it is one of the best electron attachers known. In Table I, SF_6 is one of the few compounds for which simple attachment (attachment without dissociation) was observed. The ratio of SF_5^-/SF_6^- was less than 1/20, which is in agreement with Hickam and Fox [21], and it is tempting to explain the ineffectiveness of SF_6 as an inhibitor by the fact that too few residual radicals are formed. However, this may not be a valid explanation, since Hickam and Berg [22] found that the ratio of SF_5^-/SF_6^- depends on temperature, being .25 at 80°C and 1.5 at 280°C. The SF_6^- ion is formed with excess energy and is unstable. Since the SF_6 molecule is large and has many bonds, it is able to hold together for a time in its excited state. But eventually some SF_6^- ions stabilize by ejecting an electron or F atom. The fact that SF_6 does not inhibit combustion suggests one or more of the following:

1) Most SF_6^- ions are stabilized in flames by ejecting an electron (i.e., SF_5^- and F are not formed);

2) The delay between attachment and dissociation to SF_5^- is sufficient for the negative ion to pass out of the reaction zone;

3) The increased ratio of SF_5^-/SF_6^- at flame temperature, which is expected from the work of Hickam and Berg, does not materialize;

4) The residual free radical, F., for some unknown reason does not react with the free radicals in the flame;

5) The negative ions, SF_6^- and SF_5^-, do not react with the free radicals in the flame.

Of course, reaction (1) cannot take place in flames which have no free electrons. Such is the case in Hydrogen flames. Bulewicz and Padley [17] found no measurable trace of ionization in Hydrogen, Carbon Monoxide, Hydrogen Sulfide and Carbon Disulfide flames burned with Oxygen. They conclude that the electron density is at least three orders of magnitude less than in hydrocarbon flames. Ion formation in H_2-O_2 flames is directly proportional to hydrocarbon impurity concentration [18]. It is also true that, as a rule, inhibitors are less effective when used with Hydrogen-Oxygen flames than in Hydrocarbon-Oxygen flames. Lask and Wagner [5], for example, published curves showing that 35% by volume of C_2F_3Cl must be added to H_2- air mixture to make it non-flammable for all H_2-air mixtures, but that only 14% is needed for n-hexane - air mixtures, and 9% for Benzene - air. They also note that "with H_2 as fuel, $Fe(CO)_5$ is less effective (as an inhibitor) than with hydrocarbons." Creitz [8] has published curves showing that, for a given oxygen concentration, much more CF_3Br and CH_3Br is needed to extinguish hydrogen flames than hydrocarbon flames. This inhibitor ineffectiveness in hydrogen flames cannot be due to a dearth of flame free radicals, since it is known [19] that large amounts of H, OH, and O are produced in the reaction zone of the hydrogen flame. It must be due to a deficiency in electrons.

The situation is not so clear with CO - O_2 flames. Simmons and Wolfhard [13] report that in CO and air flames, "the amount of methyl bromide which can be introduced into carbon monoxide before the flame is extinguished is very large." Creitz [8] agrees that CH_3Br is ineffective in CO flames, but found CF_3Br to be quite effective.

If reaction (1) is the first step in inhibition, the inhibiting compounds must not only exhibit high electron attachment, but the attachment cross section must be high at the electron energies characteristic of electrons in a flame. As mentioned before, the average electron energy in flames is thought to be below 1 electron volt. This is also the energy range where the attachment cross sections are high for inhibitors [22][24].

Compounds such as CH_3Br, CF_3Br, and CF_3Cl are inhibitors [25][26], and attach at the right energies [27][10]. It is surprising, then, that CH_3Cl is not an effective inhibitor [26]. In terms of electron attachment, the explanation is clear. No negative ions are produced in CH_3Cl until an electron energy of 10ev is reached (well above the energies of flame electrons). Thus attachment similar to equation (1) cannot take place. The same can be said for CH_3F (negative ion appearance potential of 12.4 volts [27]) and CF_4 (negative ion appearance potential of 4.5 volts [10]). Neither CF_4 nor CH_3F are chemical inhibitors.

Attachment cross section curves generally have a narrow peak at low electron energy, indicating a resonance attachment process. With some inhibitors, there is a second, somewhat broader peak which follows the initial one [22] [24]. In terms of the flame system, this means that a significant number of electrons must have energies at which the cross section peaks occur if reaction (1) is to be important.

From the definition of cross section it can be shown that:

$$\frac{\text{attachments}}{\text{cm}^3 \cdot \text{sec}} = n_o \cdot \text{mole fraction of inhibitor} \cdot \int_0^\infty \sigma(v)\rho(v)\, v\, dv \quad (5)$$

where: $n_o = 4 \times 10^{18}$ molecules /cm^3 at 1800°K and atmospheric pressure

$\sigma(v)$ = attachment cross section, which is a function of velocity, v.

$\rho(v)\, dv$ = number of electrons having velocity between v and $v+dv$ per cm^3.

If reaction (1) is the first step in inhibition, then the effectiveness of a particular inhibitor depends on the electron energy distribution in the flame to which the inhibitor is added. There are several observations in the literature which seem to support this idea.

Creitz [8] shows graphs in which the effectiveness of CF_3Br and CH_3Br can be compared in Hydrogen-air and Hydrocarbon-(i.e., Ethane, Propane, and Butane) air flames. CH_3Br is the better inhibitor in the hydrogen flame, but CF_3Br is more efficient in the Hydrocarbon flames. The hydrogen flame temperature is greater than that for the hydrocarbons [28], and it is reasonable to expect the electron velocity distribution, $\rho(v)$, to be shifted to higher values of velocity. Thus the greater efficiency of CH_3Br in the Hydrogen flame can be accounted for if the attachment cross section peak for this compound occurs at slightly higher velocity (or energy) than for CF_3Br. The energy required for attachment to take place is $D(x-y) - EA + \Sigma$, where $D(x-y)$ is the dissociation energy of the xy bond, EA is electron affinity, and Σ is the kinetic energy and energy of excitation of the products of reaction. In comparing the attachment process for CH_3Br and CF_3Br, EA is the same since the electron attaches to a Br atom in both cases, and it is assumed that Σ is also similar for the two compounds. However, Dibeler et al [10] have reported that $D(CH_3-Br) - D(CF_3-Br) = 3$ kcal. Thus electron attachment in CH_3Br does take place at slightly higher electron energy.

Another observation indicating the possible importance of the relative values of $\rho(v)$ and $\sigma(v)$ has been made by Bonne, Jost and Wagner [6]. They report the effectiveness of $Fe(CO)_5$ on hydrocarbon-air flames is much greater than on hydrocarbon-oxygen flames, which of course, are hotter and probably have a higher average electron velocity. It would be interesting to know if the attachment cross section peak for $Fe(CO)_5$ occurs at the low side of the electron velocity distribution so that the product of $\sigma(v)\rho(v)$ under the integral sign in (5) decreases as $\rho(v)$ shifts to higher values of velocity for the hotter oxygen flame.

Bonne et al also published data showing that flame speed does not change significantly with pressure in the 0.1 to 1.0 atmosphere range. This suggests that flame temperature, and thus average electron energy, also remains essentially unchanged. At pressures below 0.1 atmosphere, the flame speed of Bonne's methane-air flame did increase. However, it has been reported [29] that the relative effectiveness of 7 inhibitors is the same at both 1 atmosphere and 0.01 atmosphere flames, suggesting that even at 0.01 atm, the electron energies in flames have not changed by a large amount.

Although the relative effectiveness of inhibition does not seem to change with pressure, the absolute value of effectiveness has been found to change. Bonne et al [6] report that the efficiency of $Fe(CO)_5$ as an inhibitor decreases with decreasing pressure in the 1.0 to 0.1 atmosphere range. This effect can be explained by a reduction in reaction rate. The electron concentration is proportional to pressure [17], so the relative concentrations of inhibitor and electrons is unchanged. However, the reaction rate of both the electron attachment process and the reaction with the flame free radicals which follows is reduced, thereby diminishing inhibition.

3.2 Linearity of Inhibited Flame Speed Curves

Define an average attachment cross section $\bar{\sigma}$, so that:

$$[e]\ \bar{v}_e\ \bar{\sigma} = \int_0^\infty \sigma(v)\ \rho(v)\ v\ dv$$

where:

$[e]$ = electron density = $\int_0^\infty \rho(v)dv$

$\bar{v}_e$ = average electron velocity = $\dfrac{\int_0^\infty \rho(v)\ v\ dv}{\int_0^\infty \rho(v)\ dv}$

$\sigma(v)$ and $\rho(v)$ are the same as defined in equation (5).

Then: $$\bar{\sigma} = \frac{\int_0^\infty \sigma(v)\ \rho(v)\ v\ dv}{\int_0^\infty \rho(v)\ v\ dv}$$

If inhibitor concentration (n_o x percent inhibitor added) is written as $[I]$, then equation (5) can be written as:

$$\frac{\text{attachments}}{\text{cm}^3 \cdot \text{sec}} = k\ [e]\ [I] \qquad (6)$$

where $k = \bar{v}_e\ \bar{\sigma}$. Equation (6) has the form of a rate equation for reaction (1) with $[I]$ being the general term for $[CF_3Br]$. Equation (6) also gives the number of residual radicals (and negative ions) being produced per second per cm^3. Since it is proposed that the residual radicals (and/or negative ions) are responsible for inhibition by reacting with flame free radicals, it is reasonable to assume that the speed of an inhibited flame is equal to the uninhibited flame speed minus a term which is proportional to the number of attachments per cm^3 per sec:

$$S = S_o - k'\ [e]\ [I] \qquad (7)$$

where S_o is the speed of an uninhibited flame and k' is a new constant.

As long as [I] is small so that [e] in equation (6) remains essentially constant, the attachment per volume per second is linear with [I]. The reduction in flame speed is thus also a linear function of inhibition concentration. However, at higher inhibitor concentrations, the rate of electron attachment becomes comparable with the rate of electron production. When this happens, an increase in inhibitor concentration, [I], results in a decrease in electron concentration, making equations (6) and (7) nonlinear.

This behavior is observed experimentally. Garner, Long, Graham, and Badakhshan [30] found that "the reduction in burning velocity is almost linear with increase in concentration of additive (although there is some evidence of a slight falling off in effectiveness as the concentration increases)." Bonne, Jost and Wagner [6] reported linear decrease in flame speed with addition of up to 0.3 Mole % of $Fe(CO)_5$, and up to 0.95 Mole % of Br_2. Lask and Wagner [5] used large enough inhibitor concentration for the non-linearity to be clearly evident. The interesting thing is that generally the best inhibitors at low additive concentrations also become nonlinear at the lowest inhibitor concentration. The sketch in Figure 1 illustrates this point. Compound "A" is the best inhibitor at low additive concentrations, since it leaves the flame speed axis with the greatest negative slope. Compound "A" also becomes nonlinear at smaller concentrations than either "B" or "C". Data presented in Lask and Wagner's report actually shows this behavior.

If reaction (1) is important, the best inhibitors should become nonlinear first. They are the best electron attachers, and therefore they cause an exhaustion in free flame electrons first, resulting in the nonlinearity.

The next question is whether the nonlinearity occurs at the expected additive concentration, i.e., the concentration at which the electron density is significantly reduced. In order to show that this is, in fact, the case, a short discussion of the origin of electrons and negative ions in hydrocarbon flames is necessary.

It is generally agreed that ionization in a flame occurs by the chemi-ionization process. In chemi-ionization, ions are produced simultaneously with some chemical rearrangement of the reacting bodies. The reaction most often mentioned is:

$$CH + O \rightarrow CHO^+ + e^-$$

Calcote et al [16], in a study of the origin of negative ions in flames, concludes that "The main source of negative ions is dissociative attachment of electrons to $C_2H_2O^*$, with possibly, some contribution from electron attachment to O_2, O and/or OH." The important point here is that negative ions probably are not formed in the primary ionization process of the fuel fragments.

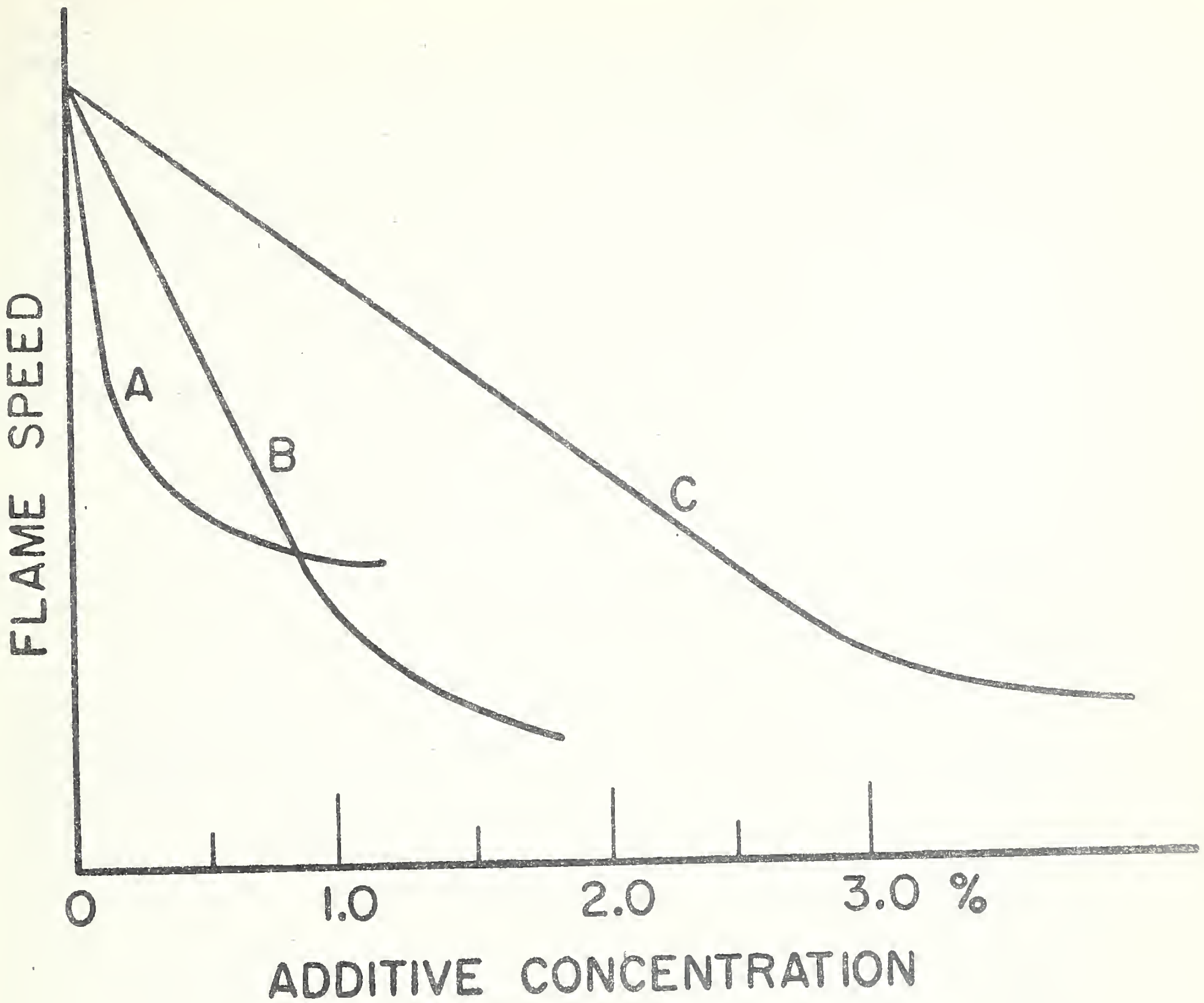

Fig. 1. A sketch showing how the onset of nonlinearity occurs at lower additive concentrations for the better inhibitors. See report by Lask and Wagner [5] for actual data.

Calcote [16] observed that negative "ions appear in addition to, not in place of, the ions previously observed in the clean flame." Presumably this is at additive concentrations of less than 1%, because Feugier and Van Tiggelen report [15] that when chlorine compound concentration reaches the order of 1%, all negative ions which appear in normal flame are replaced by Cl^-. It would appear that negative ions normally found in hydricarbon flames are formed by attachment in clean flames, where the supply of electrons is abundant. But they are unable to form when all or most of the free electrons have attached to additives. Therefore, based on Feugier and Van Tiggelen's observation, most of the electrons are used up at about 1% additive concentration. This conclusion fits Lask and Wagner's [5] data. The flame speeds of most of the compounds which they studied become nonlinear in the 0.5 to 1% range of additive concentration.

The idea that the free electron density in hydrocarbon flames is significantly reduced with the order of 1% inhibitor added (i.e., rate of electron attachment is comparable to rate of electron production at 1% additive) can be confirmed somewhat quantitatively by using equation (6). First a reasonable value for [e] will have to be found. If the conclusion drawn above is correct, that the primary ionization process in hydrocarbon flames involves positive ions and electrons (no negative ions) and that the negative ions found in a clean flame are formed only if the electron supply is not depleted by additives, then it can be concluded that the number of electrons per cm^3 which are available for attachment to inhibitor molecules is equal to the number of positive ions per cm^3. This number varies in the literature from 10^9 ions /cm^3 to 10^{13} ions/cm^3 [31] [34], so 10^{11} electrons per cm^3 will be used as a reasonable value for [e] in equation (6).

The reaction constant, k, in equation (6) was found to equal the average electron velocity times the average electron attachment cross section. Using plausible values for v_e (0.2 electron volts or about 10^7 cm/sec and σ_6 (10^{-17} cm^2 [24]), k is equal to 10^{-10} cm^3/sec. Then at [I] equal to 10^{16} molecules/cm^3 (or about 1% inhibitor at flame temperature), there are about 10^{17} attachments per sec per cm^3.

This is comparable to the rate of election (or positive ion) production found in the literature. Calcote published a production rate of 10^{15} ions/cm^3/sec [32]. With some reservations, Van Tiggelen arrives at a value of 10^{17} to 10^{20} ions (or electrons) per cm^3 per sec [31]. The agreement seems close enough to support the proposition that the nonlinearity in flame speed reduction curves beginning at about 1% is due to the reduction in the free electron supply.

3.3 Some Inhibitors Burn

In the 6th Combustion Symposium, Garner, Long, Graham, and Badakhshan [30] observed "The presence of halogenated methane as additive in the fuel/air mixture leads to two effects: the first is that of additional fuel (when part of the additive molecule is combustible) which causes an apparent shift in the position of the burning velocity vs mixture strength curves, while the second is the marked inhibiting effect on flame propagation." Others have also noted that some inhibitors acted as fuel, especially in lean flames [8], [26]. These observations clearly support the theory presented. The residual radical from CH_3Br, for example, would be CH_3. Upon reaction with H radicals in the flame, CH_4 would be formed. Thus, the net result of adding CH_3Br would be a decrease in H concentration and an increase in methane concentration (i.e., an increase in fuel concentration).

4. Summary

None of the observations which have been discussed in this paper are conclusive. However, taken together they appear to justify serious consideration of the theory that electron attachment is a necessary first step in inhibition. It appears that the limiting factor in inhibitor effectiveness at higher concentrations is the supply of electrons in flames. This is not the total supply of electrons, but only those which have the proper energy for electron attachment to the inhibitor molecule.

An experiment can be performed which, if successful, should provide evidence on the importance of electron attachment in inhibition reactions. At the same time, such information should have practical value by suggesting more effective extinguishing agents. If two inhibitors can be found with (a) slightly different electron attachment energies yet still within the energy distribution of flame electrons, and (b) which can be mixed without reacting with one another, then two "slices" of electrons would be removed from the electron energy distribution instead of one. A mixture of these compounds used to inhibit a flame should thus result in the flame speed reduction vs inhibitor concentration curve remaining linear for larger concentrations than if the compounds had been used separately, thereby resulting in a greater reduction in flame speed.

TABLE I: SUMMARY OF RESULTS

SAMPLE	NEGATIVE IONS OBSERVED	SAMPLE PURITY AND SUPPLIER		REFERENCE
1. CCl_4	Cl^-	(Baker 1512)	(B)	(2) (3) (10)
2. CF_2Br_2	Br^-	CF_2Br_2 - 98.9% $CFCl_2Br$ - 1.1%	(M)	
3. CF_2Cl_2	Cl^-	CF_2Cl_2 - 99.8% Hydrocarbons - 0.1%	(M)	(3)
4. CF_3Br	Br^-	CF_3Br - 99.8% C_2HF_5 - 0.1%	(M)	(4)
5. $CHBr_3$	Br^-	Stabilized with Diphenylamine (Eastman 45)	(E)	
6. $CHCl_3$	Cl^-	Spectro Grade (Eastman S 33)	(E)	
7. $CHFCl_2$	Cl^-	$CHFCl_2$ - 99.7%, CCl_3F -0.1% $CHClF_2$ + CH_2F_2 - 0.2%	(M)	(3)
8. CH_2Br_2	Br^-	(Eastman 1903)	(E)	
9. CH_2BrCl	Br^-	(Eastman 5698)	(E)	
10. CH_3Br	Br^-	CH_3Br - 99.7% CH_3Cl - 0.3%	(M)	(5)
11. CH_3I	I^-	(Eastman 164)	(E)	(5)
12. C_2H_4BrCl	Br^-	(Eastman 567)	(E)	
13. C_2H_5Br	Br^-	Ether Free (Eastman 114)	(E)	

TABLE I: SUMMARY OF RESULTS (continued)

SAMPLE	NEGATIVE IONS OBSERVED	SAMPLE PURITY AND SUPPLIER		REFERENCE
14. $C_8F_{16}O$	$C_8F_{16}O^-$	3M Chemical Co. label FC-75 Reported to be a cyclic ether		(6)
15. ClO_3F	ClO_3^- F^-	ClO_3F - 98% Inerts (including Moisture)-2%		(2)(3)
16. $Fe(CO)_5$	$Fe(CO)_4^-$	Obtained from City Chemical Co.		
17. PCl_3	Cl^-	SO_4-0.0005%, Fe-0.0003% Heavy Metals - 0.0005%		
18. $POCl_3$	$POCl_2^-$ Cl^-	SO_4-0.01%, Fe- 0.001% Heavy Metals - 0.002%		
19. SF_6	SF_6^- SF_5^-	SF_6 - 98%	(M)	(3)(7)(8)
20. $TiCl_4$	Cl^-	(Fisher T 308)	(F)	(9)

(B) Obtained from Baker Chemical Co.

(E) Obtained from Eastman Distillation Products Industries.

(F) Obtained from Fisher Scientific Co.

(M) Obtained from Matheson Co.

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