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Seventeenth Quarterly Progress Report

on the

Mechanisms of Fire Ignition and Extinguishment

by

E. C. Creitz

Covering the period August 1, 1963 to October 31, 1963

for

Bureau of Ships

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1. Summary

A review of background information leading up to the construction of the mass spectrometer is given. Negative ion masses produced from SF_6, CCl_4 and ClO_3F have been measured. Increased accuracy in the calibration factor has been attained altho drift has not been completely eliminated.

2. Review of Background Information

Reactions between electrophylic and electrophobic species in flames are believed to be important from the standpoint of the mechanisms of extinction of flames. This view is the result of the work of Creitz (1) who noticed the correlation between the efficiency of halogenated hydrocarbons as extinguishing agents and the yield of negative ions by electron attachment in the mass spectrometer, and that of Lee (2) who studied a large number of compounds including non-halogen compounds, such as iron pentacarbonyl and lead tetroethyl, and concluded that all compounds which are known to be inhibitors will attach low energy electrons. However, there are other compounds such as SF_6 which attach electrons and which are known to have little or no effect on flame reactions. The present work in construction of the new type of mass spectrometer is directed toward its eventual use in determining the differences in the attachment mechanism between inhibiting and non-inhibiting electron attaching gases. There is some evidence in the literature that attachment of electrons by compounds which dissociate to give negative halogen ions produces inhibition reactions in flames. In this case the energy of the attaching electron is at least as large as the dissociation energy and the electron ends up attached to the halogen atom which was dissociated from the original molecule, as in the following:

$$CF_3Br + \varepsilon(1.5\ ev) \longrightarrow CF_3 + Br^-$$

The detachment of the electron from the Br^- ion requires in the order of 3.5 ev energy so that the above reaction is, essentially irreversible.

On the other hand, compounds like SF_6 can form molecular negative ions such as SF_6^- and SF_5^- which have detachment energies comparable to those for attachment. The mass spectrometer is to be used to try to connect an attachment mechanism such as one of the above, to the inhibition process.

Other work of interest which is not financed from this project includes, (1) further studies of the attachment of electrons by measurement of the temperature coefficient of attachment and (2) a study of the products of combustion of inhibited flames. The latter study is an attempt to trace the history of inhibitor molecules in passage thru a flame. Private conversations with others working in the field of chemical kinetics has elicited the opinion that ionic processes are indeed important in the inhibition of flame reactions.

3. The Mass Spectrometer

Optimum focusing settings were determined and no difficulty was experienced in measuring the masses of negative ions obtained from SF_6, CCl_4 and ClO_3F. The data indicated that it would not be necessary to shield the filament from the gas to avoid thermal decomposition of the gas, as had previously been thought might be necessary. Electrons were removed from the stream of negative ions by the use of a weak magnetic field from a permanent magnet.

A better way for determination of the calibration factor was worked out, with the help of data analysts of the NBS, so that it is now believed that an error of ±0.1 can be achieved, exclusive of drift, which has not yet been measured.

When appearance potentials measurements are made, it is important that the electron current from the filament remain constant. Efforts are being made to automatically control the filament current. This seems not to be as simple as it appears and efforts are being continued to produce such a regulator.

4. References

(1) E. C. Creitz, "Inhibition of Diffusion Flames by Methyl Bromide and Trifluoromethyl Bromide Applied to the Fuel and Oxygen Sides of the Reaction Zone", J. Res. NBS, 65A, 389 (1961).

(2) T. G. Lee, "Electron Attachment Coefficients of Some Hydrocarbon Flame Inhibitors", J. Phys. Chem., 67, 360 (1962).