SURVEY OF CHEMICAL INHIBITION IN FLAMES

Raymond Friedman

Atlantic Research Corporation, Alexandria, Virginia

When a fire is extinguished by addition of a third substance to fuel and air, the mechanism of the effect obviously may be either blanketing, i.e. separation of the fuel from the air, or cooling, i.e. reducing the flame temperature to the point where flame kinetics is too slow to maintain combustion. However, either of these effects would depend on the specific nature of the third substance only through the generally well known physical and especially thermal properties of that substance. Practical experience has shown that some extinguishing agents are significantly more effective than can be accounted for on this basis, and this finding has led to the belief that chemical inhibition may play a key role in fire extinguishment. Evidence for this view will be briefly reviewed here. A more detailed review made in 1957 is available (1).

The most widely known agents believed capable of chemical inhibition of flames of organic fuels fall in two classes: (a) volatile substances containing bromine or iodine; (b) alkali metal salts (except lithium). While one might think it would be relatively simple to demonstrate the superiority of these over other chemical substances, if such superiority exists, by making comparative pan-fire extinguishment tests, this has not proven to be so. One difficulty is the notoriously poor reproducibility of pan-fire experiments, probably largely due to the random nature of the free convective gas motion around such fires. Another complication is that the bromine compounds may themselves be fuels (e.g. methyl bromide) or oxidants (e.g. elemental bromine). In the case of salts, there are problems of knowledge of surface area and degree of dispersion, and the difficulty of knowing the number of salt particles present per unit volume of burning gases. These problems notwithstanding, results of many fire-extinguishment studies tend to show the superiority of the above-mentioned classes of compounds over other substances of similar physical properties.

The combustion scientist, however, would prefer more than statistical evidence from model fire studies. He has made detailed measurements over the past eighty years of flammability limits, burning velocities, and quenching distances of premixed combustible gases at rest or in steady streamline flow, and he has at least partially reliable theories which qualitatively relate these flame properties to the "first principles" of chemical kinetics and gas kinetics. It is only in the past few years that measurements of this kind have been utilized systematically to examine the question of flame inhibition.

Let us first consider flammability limits. For example methane-air mixtures containing less than roughly five or more than roughly fourteen per cent methane are not flammable, the stoichiometric composition lying in the middle of this range. Upon adding additional nitrogen to any flammable methane-air mixture, a point is reached where it is no longer flammable. Finally, thirty-eight per cent additional nitrogen is enough to render all methane-air mixtures nonflammable. While the mechanism causing such a limit is not rigorously known, most combustion scientists would accept the following explanation. Addition of excess diluent, fuel, or oxidant reduces the flame temperature, and hence the rate of heat generation by chemical reaction, according to the Arrhenius law. The rate of heat loss from the flame to the cold surroundings also decreases, but not as much. Thus, heat-loss rate tends

to overtake heat-generation rate as the flame is diluted. The effect is amplified by the fact that as the chemical reaction time increases, in the cooler flame, there is now more time for heat loss from the reaction zone to occur. Thus a finite limit of flammability is predictable mathematically, governed primarily by the magnitudes of the chemical reactivity and the heat-loss rate. (The relative importance of convective and radiative heat loss is not yet well understood.)

Now, if elemental bromine vapor (2) is added to methane-air, 2.45 mole per cent is sufficient to render all mixtures nonflammable, compared with 38 mole per cent nitrogen for the same effect. On this basis bromine is some 15 times as effective as nitrogen in extinguishment on a molecular basis, a result which cannot be explained except as a specific chemical effect, presumably inhibition. It follows from the above finding that one bromine molecule can prevent the combustion of four methane molecules. Many other examples of narrowing of the flammability range by additives have been reported.

Let us now consider burning velocity, which is the idealized rate at which a flat combustion wave would propagate through an initially stationary combustible mixture. This velocity may be deduced, to an accuracy of a few per cent, from the knowledge of the shape of a stabilized laminar flame in a known flow field, as a Bunsen burner provides. The magnitude of the burning velocity is determined by the interaction of two important parameters, the chemical reactivity in the flame and the transport properties of the mixture. Since the latter are influenced only slightly by small additions of possible inhibitors, we have a convenient means of measuring inhibition of the chemical reactivity quantitatively by observing burning velocity.

Consider the data below, which show systematic measurements of reduction in burning velocity by a series of volatile bromine and other halogen compounds:

ADDITIVE REQUIRED FOR 10% REDUCTION OF
STOICHIOMETRIC METHANE-AIR BURNING VELOCITY (3)

additive	number of halogen atoms	molecules additive required per 100 molecules CH_4
HBr	1	1.8
CH_3Br	1	1.6
CF_3Br	1	1.2
Br_2	2	0.83
CH_2Br_2	2	0.81
CF_2Br_2	2	0.85
$CHBr_3$	3	0.55
CH_3Cl	1	4.9
CH_3Br	1	1.6
CH_3I	1	1.7

Note that one molecule of bromine added to 100 molecules of methane (and 900 molecules of air) is more than enough to produce a ten per cent reduction in burning velocity. It can be shown that the burning velocity varies with the square root of chemical reactivity, so this corresponds to a reduction of 21 per cent in chemical reactivity. Such a small addition could not affect the flame temperature significantly, so the effect must be a chemical inhibition. Note that all seven of the bromine compounds show similar effects, the strength of the inhibition being almost directly proportional to the number of bromine atoms per molecule. Note further that iodine is comparable with bromine while chlorine is much less effective.

Consider now the greater variety of chemical substances tested in another investigation:

ADDITIVE REQUIRED FOR 30% REDUCTION OF STOICHIOMETRIC HEXANE-AIR BURNING VELOCITY (4)

Additive	molecules required per molecule hexane
CO_2	4.05
N_2	4.05
Cl_2	1.54
Br_2	0.33
$TiCl_4$	0.09
PCl_3	0.07
$Pb(C_2H_5)_4$	0.034
$Fe(CO)_5$	0.033

Here the fuel vapor is hexane instead of methane and data are reported on the basis of a 30 per cent instead of a 10 per cent reduction in burning velocity. Note that the most effective substance, iron pentacarbonyl, is more than 100 times as effective as the least effective substances, carbon dioxide and nitrogen. Bromine occupies an intermediate position in this list. New data (5) show that iron pentacarbonyl is such a powerful inhibitor that one molecule, added to 10,000 molecules of a stoichiometric methane-air mixture, reduces the burning velocity by 25 per cent.

It must be mentioned that pure iron pentacarbonyl is flammable in air, so it would hardly be capable of extinguishing an open fire unless used in combination with some other agent. Nevertheless the powerful inhibiting effect produced by traces is highly suggestive.

We turn now to the third premixed flame property frequently measured by combustion scientists, quenching distance. This is the closest distance of approach of a flame to a cold wall, and is readily determined to about one per cent accuracy by observing the minimum width of a rectangular or circular channel through which a flame can propagate. As does burning velocity, quenching distance depends on transport properties and chemical reactivity. The minimum pressure at which a flame would propagate through a stoichiometric propane-air mixture in a 3.73-diameter tube has been reported (6) to increase from 46 mm Hg to 80 mm Hg upon addition of 0.1 mole per cent methyl iodide, or one molecule of inhibitor per 40 molecules of propane. Since quenching distance of propane-air is nearly inversely proportional to pressure, this result is about equivalent to an 80/46 increase in quenching distance at constant pressure. Similar effects were observed with bromine-containing agents, while carbon tetrachloride was much less effective. Another investigator (7) has measured the depth of flame penetration into a tapered tube of gradually decreasing diameter, the diameter of the tube at the position of furthest flame penetration being taken as the quenching distance. An 8 per cent increase in quenching distance is reported to be produced by addition of one molecule of bromotrifluoromethane per 1000 molecules of stoichiometric methane-air, hydrogen bromide being not quite as effective.

The above examples, based on precise measurements of flammability limits, burning velocities, or quenching distances of premixed hydrocarbon-air mixtures, clearly show that trace quantities of certain gaseous substances can substantially reduce flame reactivity and thus make extinguishment easier. Similar data, although not so quantitative, are available for effects of suspended sodium and potassium salts on flames.

Let us now examine what is known about the chemical mechanisms by which these agents act, a necessary preliminary to rational development of more potent or less toxic agents.

Considering first the bromine and iodine inhibition, we note that the effectiveness of a variety of carrier molecules correlates well with the number of halogen atoms per molecule, so it is reasonable to assume that breakdown to some simple halogen-containing molecule occurs in the flame, the latter being responsible for the inhibition. In the case of bromine inhibition, Br_2 will not exist at flame temperature, so Br and HBr are the candidates. However, to inhibit the flame, it seems probable that the inhibitor must deactivate the most abundant chain-carrying radicals present, H and OH. Monatomic Br could not do this except by slow three-body processes while HBr can easily react by a rapid two-body process, e.g.,

$$H + HBr \rightarrow H_2 + Br \quad \text{or} \quad OH + HBr \rightarrow H_2O + Br$$

with inhibitor regeneration by hydrogen abstraction:

$$Br + HR \rightarrow HBr + R \quad .$$

The radical R must be presumed less reactive (or less capable of upstream diffusion) than the H or OH it replaces. Since H has the unique ability to lead directly to chain-branching via

$$H + O_2 \rightarrow OH + O$$

any inhibiting mechanism capable of removing H (or OH, since $OH + CO \rightleftharpoons H + CO_2$ is rapid) looks promising. The reaction of H with HBr to form H_2 however is not a satisfying explanation of inhibition since the H_2 would rapidly oxidize, giving more H atoms. Thus OH radicals may be the key species inhibited by HBr. This kind of speculation was first published by Rosser et al. (3), and others who have considered the problem generally utilize this approach as a working hypothesis. However, neither the theory of chain-reaction-governed flames nor knowledge of individual rate constants is sufficiently advanced to permit a theory like this to be proved. Rosser et al. (3) have observed that the 3064 Å emission line from excited OH decreased in intensity as bromine was added, but confirmatory evidence obtained by observing unexcited OH in absorption would be highly desirable.

According to the above ideas, HI should behave similarly to HBr, and HCl and HF are too stable to react rapidly with free radicals, so the behavior of the entire halogen family is accounted for if one accepts the foregoing type of mechanism.

Considering now the inhibition produced by other substances, especially metal compounds, we find much less understanding. The mere fact that powerful inhibition can occur is good evidence that chain carriers are being taken out of circulation, and the further fact that hot fuel-oxygen flames are less susceptible to inhibition than cooler fuel-air flames is readily attributed to the much higher radical concentrations believed present in the hotter, faster-burning flames, making them harder to inhibit. To progress beyond this point to specific mechanisms is difficult. Metal atoms might react with O, OH, or H to form oxides, hydroxides, or hydrides, or metal atoms might remove energy from active species by becoming electronically excited and then radiating. When the metal-containing substance is added in dispersed condensed-phase form, there is a choice between assuming surface reaction or vaporization. A paper in this symposium (8) suggests that vapor reactions are the important ones. Much more research is needed in this area.

Finally, attention must be given to the problem of relating information on inhibition of chemical reactivity in a premixed flame to the extinguishment of a fire, which is more nearly a diffusion flame. The rate of combustion in a

diffusion flame is determined by fuel-air mixing rate for a gaseous fuel, or by rate of heat transfer from flame to fuel supply for a slowly volatilizing liquid or solid fuel, and does not depend on chemical kinetics, generally speaking. Thus, introduction of an inhibitor which would cause a moderate reduction of reactivity in a premixed flame would be expected to have no measurable effect on a diffusion flame. Nevertheless, a gaseous diffusion flame as maintained on any of several types of laboratory burners can be extinguished when a sufficient concentration of inhibitor is mixed with the air supply, the necessary concentration of inhibitor being roughly that which would extinguish a premixed flame of the same fuel. This gaseous diffusion-flame extinction process may be attributable to the presence of one or more local regions in the flame, generally at the base, which serve to anchor or stabilize the flame. Such a region, which might be very small, could contain fuel and air which mix before they burn, while in the bulk of the flame, mixing and burning are simultaneous. The inhibitor may exert its entire action in this small region. Detailed studies of this effect have apparently not been made.

A potential method for studying effects of inhibitors on diffusion flames is Potter's experiment (9) in which coaxial opposing jets of fuel and air of equal flow rates meet at a flame surface. At sufficiently high flow rates, the flame ruptures, as indicated by appearance of a hole. Effects of inhibitors on this process have not yet been reported, but such experiments are currently under way in our laboratory.

In conclusion, the fundamental knowledge of flames and inhibition thereof is sufficient to show promise that practical methods of fire control may evolve from this approach, but such knowledge is as yet quite fragmentary, and more basic research is required.

References

1. R. Friedman and J. B. Levy, WADC Technical Report 56-568, "Survey of Fundamental Knowledge of Mechanisms of Action of Flame Extinguishing Agents." 1957. Available from U.S. Dept. of Commerce, Office of Technical Services, as PB 121853.

2. R. F. Simmons and H. G. Wolfhard. T. Faraday Soc. 51, 1211-1217 (1955).

3. W. A. Rosser, Jr., H. Wise, and J. Miller, Seventh Symposium (International) on Combustion, Butterworths, London, 1959, pp. 175-182.

4. G. Lask and H. G. Wagner, Eighth Symposium (International) on Combustion, Williams and Wilkins, Baltimore, in press.

5. U. Bonne, W. Jost, and H. G. Wagner, this symposium.

6. F. E. Belles and C. O'Neal, Jr., Sixth Symposium (International) on Combustion, Reinhold, New York, 1957, pp. 806-813.

7. W. A. Rosser, Jr., S. H. Inami, and H. Wise, WADC Technical Report 59-206, "Study of the Mechanism of Fire Extinguishment of Liquid Rocket Propellants," 1959. Available from U.S. Dept. of Commerce, Office of Technical Services, as PB 151962.

8. W. A. Rosser, Jr., S. H. Inami, and H. Wise, this symposium.

9. A. E. Potter, Jr., S. Heimel, and E. Anagnostou, Eighth Symposium (International) on Combustion, Williams and Wilkins, Baltimore, in press.