# IONIC EFFECTS IN INITIATION OF IGNITION SURFACE MEDIATED SUPERBASE REACTIVITY

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## BACKGROUND

There are two generally accepted indices regarding fuel flammability. The more commonly used index is the flash point of the fuel (either closed or open cup), which is the minimum temperature for a liquid fuel to sustain sufficient levels of vapor concentration in the air immediately over the surface to produce ignition when an open flame **is** passed directly over the surface. There is therefore the requirement for a preexisting flame.

Autoignition temperature is the minimum temperature of a fuel "required to cause self-sustained combustion, independently of the heating or heated element." (Since the term "Autoignition Temperature" does not directly evoke the concept of surface effects, the synonymous term "hot surface ignition temperature" [HSIT], or more simply ignition temperature. will instead be used throughout this paper. which will delve principally on effects of surfaces on autoignition.) In this determination, there is no open flame involved in the ignition. Ignition temperatures are typically determined by applying minute portions of the fuel onto a hot surface and waiting for **up** to 10 minutes until ignition is observed (either visually or with thermoelectric sensors). If there is no ignition, the process is repeated with increasing temperatures, until ignition is finally achieved. There are a number of flame processes, including hot-flame ignition (as indexed hy autoignition temperatures (AIT), accompanied by a "rapid, self-sustaining ... readily visible yellow or blue flame"); cool-flame ignition ("relatively slow, self-sustaining barely luminous ... cool flames ... visible only in a darkened area"), indexed by cool-flame reaction threshold (CFT, "the lowest temperature at which cool-flame ignitions are observed"); and pre-flame reactions. indexed by pretlame reaction threshold (RTT, the lowest temperature at which exothermic gas-phase reactions are observed") [1:4-5].

The presently accepted ASTM method [2] for hot surface ignition temperature determinations tends to be inaccurate and highly subject to the method of determination. (Figure 1 diagrams the ASTM apparatus.) Recently, for example. an attempt was made at Tyndall **AFB** to repeat the previously cited [1:4-5] ignition temperature (240 °C) for JP4 jet fuel using this type of approach. and to determine this value for the much less volatile JP8. Surprisingly, the same ignition temperature was observed for both fuels, but at a much higher reading (ca. 540 ± 20 "C).

On close examination of the videotaped results of these experiments, our group was able to note several interesting previously unidentified features. Thus, after application of the liquid fuel drop onto the hot stainless steel surface, a dark envelope was observed to expand outward from the point of application. frequently with wisps of smoke. Spots of red hot incandescence were

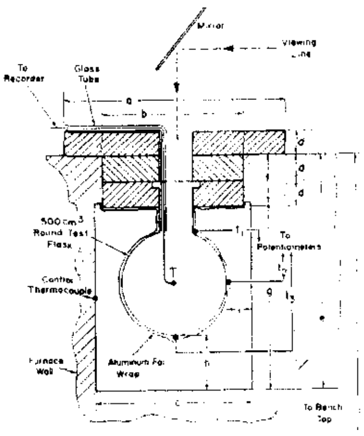


Figure 1. ASTM E569. Standard Test Apparatus for autoignition temperatures for autoignition temperatures of liquid chemicals [2].

seen to be fleeting over the surface outward from this dark patch, at heating temperatures as low as 380 °C, although red incandescence of iron formulations typically occur above 525 °C [3]. (Other workers [4, 5] have also noticed "red spot" anomalies in determining hot surface ignitions.) Blue "cool" flames were then seen to be flickering at the outer periphery of these red spots, with sudden transformation from these flickering blue flames to a sheet of white hot flame over the entire test area. Other workers have shown that combustion occurs during pre-flame periods, prior to flaming combustion, with carbon monoxide (CO) production being a prominent product ***[6]***(Table 1): In this situation (which is probably typical of many hot surface ignition temperature determinations), the liquid fuel drop vaporizes on contact with the hot surface, producing a temporary cooling effect. The fuel rich cloud spreads over the hot surface, heating to a thermal decomposition (as evidenced by frequent smoke emissions) without much oxidation. At the periphery of the fuel cloud, the fuel/air mixture becomes lean enough to afford pre-flame combustion to produce CO. CO has a much greater polarity and bonding potential than inert alkane fuel components, and would adsorb preferentially to the metal surface. Thus, the observed ignition temperature of 540 °C seen for both JP4 and JP8 could correspond to the formation of CO. (The literature HSIT value for CO is somewhat higher, 609 °C [1:25]; but the transient incandescent red spots, which do not persist long enough for true temperature registration, would be hot enough to provide CO ignition.) It is thus probably **more** often than not that conventional autoignition temperature determinations pertain not to the substrate being measured, but rather to its decomposition products.

TABLE 1. OXIDATION OF 9% $CH_4$/AIR AT 1050 °C
(ABOUT 500 °C BELOW MAXIMUM HSIT).

| Gas Present | With $Pt^0$ bar. % | With Ni" bar. % |
|---|---|---|
| Natural gas, at start | 9.1 | **8.99** |
| $CO_2$, after 8 min | 1.01 | 0.05 |
| CO, after 8 min | 0.72 | 0.50 |
| Natural **gas,** at **start** | 8.75 | *8.17* |
| $CO_2$, after 20 min | 1.96 | 0.07 |
| CO, after 8 min | 0.22 | 0.36 |

In 1991, workers at NIST devised a "Short Duration Autoignition Temperature" apparatus. In this system, "a flowing gas phase fuel stream impinges on a hot surface. ... The conventional ASTM procedure does not control the fuel/air stoichiometry. ... (In the new) apparatus ... the fuel/air stoichiometry, the nature of the hot metal surface. and the contact time are well controlled" [4:iii] (Figure 2). The results using this apparatus are obtained rapidly, with minimized contact times in which spurious decompositions can take place, and with excellent reproducibility (Figure 3); greatly increased accuracy can be seen in the resulting HSIT data. The ignition temperatures are routinely significantly higher than is the case for data derived by the ASTM system; these higher figures probably reflect actual ignition temperature profiles for all fuels, which thus are higher than previously had been suspected (Figures 3 and 4).

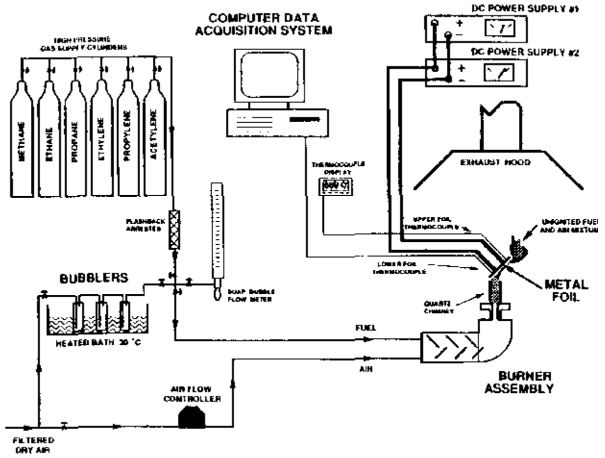


Figure 2. NIST Short Duration Autoignition Temperature Apparatus.

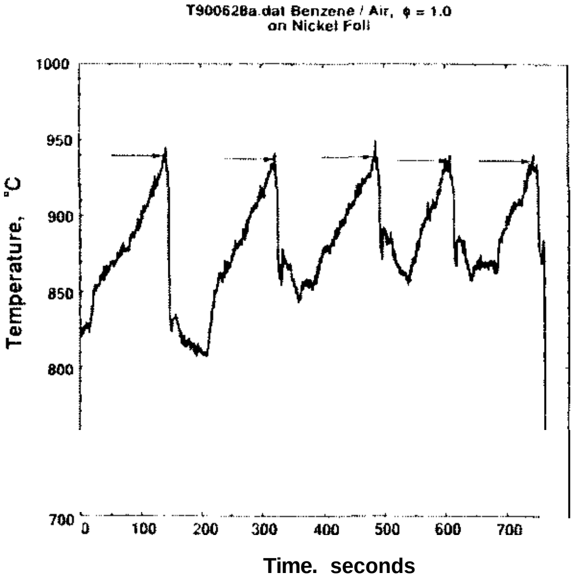


Figure 3. Temperature as a function of time for a benzene/air mixture for five repeat determinations of HSIT [4:21].

Anomalously high ignition temperatures are seen for propane and pentane. As shown in Figures 5 and 6, this may he due to recently studied "packing effects" for the lower odd-numbered alkanes (C3, C5, C7), which have lower melting points than even numbered analogs, resulting from better packing of even numbered molecules due to reduced end methyl group

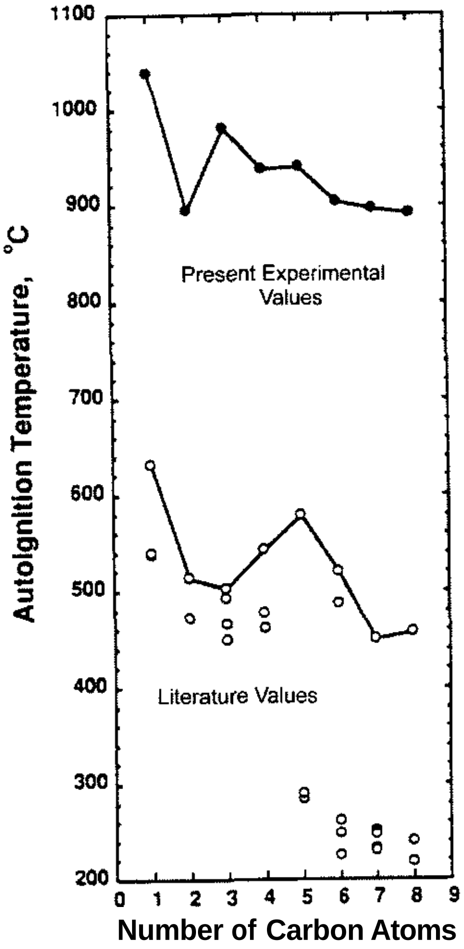
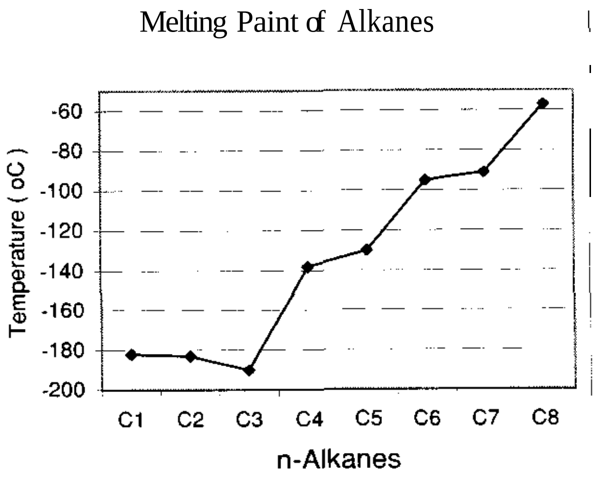
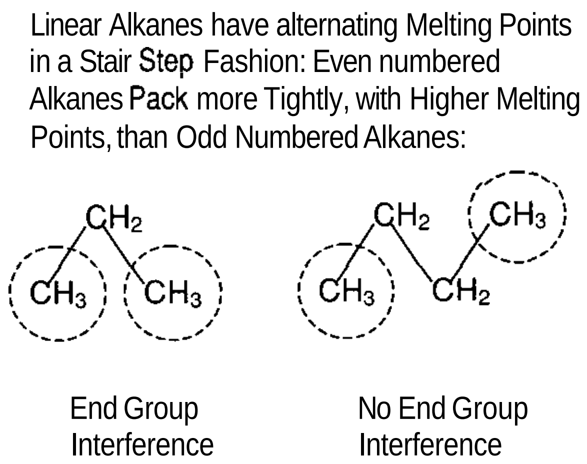


Figure 4. Comparison of measured HSIT as a function of carbon number for linear alkanes [4:29].





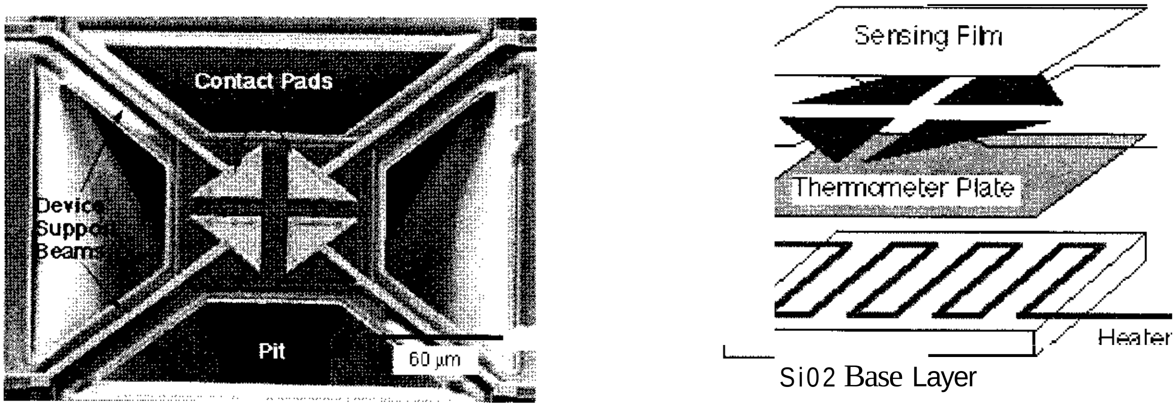
Linear Alkanes have alternating Melting Points in a Stair Step Fashion: Even numbered Alkanes Pack more Tightly, with Higher Melting Points, than Odd Numbered Alkanes:

Figure 5. Melting points of alkanes.

Figure 6. Packing effects and melting points.

repulsions [7,8]. By the same token, packing effects may be important in assembling fuel molecules on a hot surface—better packing for even numbered molecules would be consistent with the lower ignition temperatures which are indeed encountered, at least for the lower molecular weight alkanes. The general downward trend in ignition temperatures accompanying higher molecular weights may thus be attributable to better packing for longer chain molecules, and for greater statistical opportunities for interactions of adsorbed oxygen and fuel carbon-hydrogen bond moieties.

Although the NIST Short Duration Autoignition Temperature apparatus has proven to be a valuable prototype for accurate and precise measurement of ignition temperatures, there are disadvantages in terms of cost, bulk, ease of operation and general use. Recently, NIST has innovated new microthermal analysis equipment, and in particular a "MicroHotPlate" (Figure 7), capable of determining heat flow at very small dimensions **(60**µm), which is well suited for measurement of extraordinarily small thermal effects for very sensitive operations [9, 10]. Our group is proposing to miniaturize the existing NIST autoignition apparatus by incorporation of the newer NIST MicroHotPlate features, with a view to obtaining a more user friendly approach to ignition temperature determinations.



(a) (b)

Figure 7. NIST MicroHotPlate (a) and its layout (b).

## THEORY: POLARIZING EFFECTS

Although fire reaction mechanisms are emphatically of a propagating high energy free radical nature, anomalies do exist which indicate that earliest initiation stages may be of an ionic rather than free radical nature. As shown in Figure 8 and Table 2, arenes and olefins that are most susceptible to free radical attack [11] are in fact most resistant to hot surface ignition. Also, contrary to the order of reactivities in Figure 8, free radical attack on branched chain alkanes and cycloalkanes is easier than for than *n*-alkanes [11]; and cyclopentane is more reactive to free radicals than is cyclohexane [12, 13]. There is, however, better agreement with formation of carbanions for these species. Thus, initial oxidative attack on aliphatic hydrocarbons occurs most readily at primary C-H bonds, with secondary C-H bonds favored more than tertiary C-H bonds [14, 15]. This is precisely the order of stabilizing effects for carbanions [11].

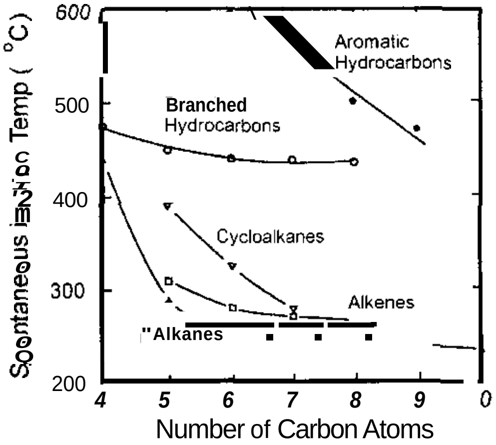


Figure 8. Ignition temperatures for various hydrocarbons [1, 14, 15, 16].

TABLE 2. EASE OF FORMATION OF GAS PHASE INTERMEDIATES [17].

| Ease of Ignition | Carbanion | Free Radical | Carbocation |
|---|---|---|---|
| Arenes - MOST Difficult | **Easy** / 379 | Easy 188 | Easy / 239 |
| Branched H/Cs -Very Difficult (comparisons are within types of intermediate) | Difficult / 419 | Difficult 193 | Easy / 231 |
| CycloAlkanes - Difficult | Difficult / 420 | More Difficult / 97 | Difficult / 250 (estimated ) |
| Alkenes - Easy | Easy / 391 | Easy / 86 | Difficult / 255 |
| Alkanes - Easiest | Difficult / 420 | More Difficult / 98 | Difficult / 250 |

(Unit: Kcal/Mole)

At first glance, the much lower energies of formation shown in Table 2, for free radical intermediates than for carbanions, would imply that free radical intermediacies would have to be operational in **all** phases of a fire. However, it must be emphasized that these data are valid only for *gas phase* considerations, which should not be expected to apply to surface chemistry. For example, it is very evident that in the gas phase the free radical process is favored for the free radical reaction (1) over the ionic gas phase dissociation (2) of **HCI** [17]:

$$\mathrm{HCl} \longrightarrow \mathrm{H}^{\bullet}\,\mathrm{Cl}^{\bullet} \qquad \mathrm{AD} = 103\ \mathrm{kcal/mole} \qquad (1)$$

$$\mathrm{HCl} \longrightarrow \mathrm{H}^{+}\,\mathrm{Cl}^{-} \qquad \Delta H_f = 186\ \mathrm{kcal/mole} \qquad (2)$$

On the other hand, impingement of gaseous HCl onto a basic surface such as NaOH obviously results in an *exothermic* ionization process. We now suggest that evidence exists to indicate that hot surfaces can function as superbases in flame initiation, and that these participate through ionic pathways in the pre-flame chemistry to form alkyl hydroperoxide intermediates (ROOH), which then quickly break down through thermal pathways to form propagating free radicals. It is interesting to note that other workers [4:30] have postulated that alkyl hydroperoxides may be central to the buildup of concentrations of radicals such as OH’, H$^\bullet$ and ‘O’ which are important species for fire propagation mechanisms.

There are important considerations based on polarizing influences, which may he exerted by the nature of the hot surface itself, and by the ambient atmosphere over the hot surface. As can be seen in Figure 9, the nature of the hot surface seems most important in governing the ignition temperature; there can be very large variations (more than 100 “C) in these values. which can be attributed only to this factor.

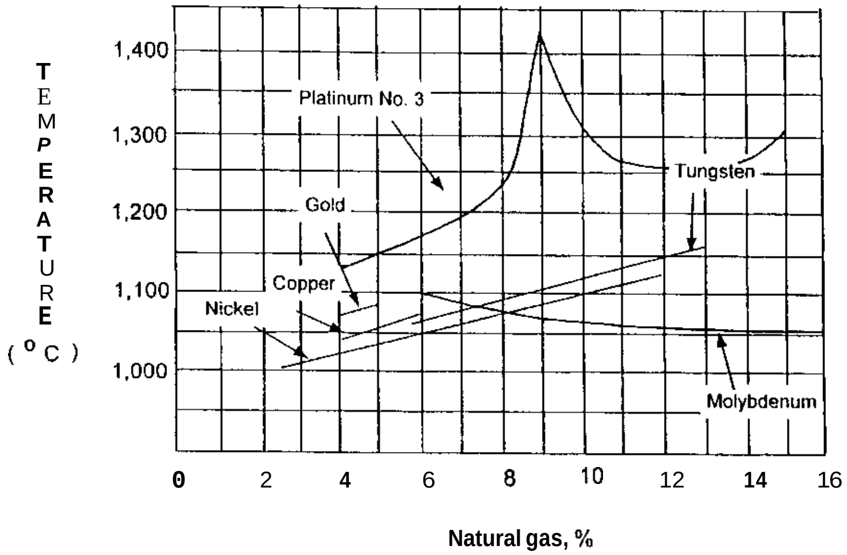


Figure 9. Ignition of natural gas mixtures (methane. ca. 80%; ethane ca. 20%) by hot metal surfaces [6]. (Note that considerable flameless combustion occurs below ignition temperatures, as seen in Table I. Note also that Pfefferle and co-workers [IS] have found that “the sharp maximum in surface temperature temperature required for gas phase ignition (for platinum) is an artifact caused by transient heating of the surface as ignition occurs.”)

Many workers (e.g., Pfefferle [19] have found important concentrations of hydroxyl, oxygen, and hydrogen free radicals on catalytic hot surfaces. Any theory involving mechanistic pathways to ignition must certainly address this phenomenon.

Table **3** provides ignition temperatures for methane in contact with the same metals as shown in Figure 9, along with electron work functions for these metals. Oxygen is known to adsorb on metal surfaces as negatively charged aggregates with electron donation from the metal to the oxygen molecule [20]. The electron work function is proportional to ease of electron migration from the metal surface, and thus to ease of polarization for adsorbed oxygen molecules. Since metals having lower work function values have lower ignition temperatures than those with higher work function values, this factor does correlate at least to some extent with ignition temperature trends.

TABLE 3. IGNITION TEMPERATURES FOR NATURAL GAS ON HOT METALS [6], AND ELECTRON WORK FUNCTIONS FOR THESE METALS [21, 22, 23].

| Metals (increase ease of ignition) | Ignition Temp. Range (°C; 5%-7% methane) | Work Function (eV) | |
|---|---|---|---|
| | | [21, 22] | [23] |
| Pt | 1155-1185 | 4.52 | 5.36 |
| **Au** | 1075-1985 | 4.46 | |
| **Cu** | 1050-1080 | | 4.65 |
| W | 1045-1075 | 4.38 | |
| Ni | 1035-1060 | 4.32 | |

**Work** function data do not always provide dependable and consistent linearity in correlation with ignition temperatures.* Other effects operate synergistically with work function effects to promote negative charge effects at hot surfaces and ionizing influences in the surface ambience. Seebeck [24, 25] and Hall current [26] effects provide for a charge transfer in heated metals, with an electron diffusion from hot to cooler metal surfaces (Figure 10). For a hot surface, there must be a hotter heat surface transferring heat to the surface: a corresponding drift of electrons with a partial negative charge builds up on the surface. The magnitude of charge (typically microvolts/°C change in temperature) may appear miniscule, but it would be anticipated that the effect for millivolt potentials for hundreds of degree temperature changes would be sufficient to promote significant polarization by interaction of partially negatively charged surfaces with thermally excited oxygen and fuel molecules adsorbed to the surface.

Repulsion of pi bonds (such as exist in arenes and olefins) can occur by the previously demonstrated partially negatively charged metal surface, with repulsion directly proportional to extent of negative charge (Figure 11) [27, 28]. The higher ignition temperatures that characterize those metals with the larger work functions can be ascribed to greater degrees of repulsion and attendant greater thermal energies required to activate the repelled oxygen and fuel molecules.

Oxyanionic surfaces such as quartz also can facilitate hot surface ignition by the strong polarization of oxygen molecules by virtue of strong attractive forces between the negative dipole of the oxygen molecule and the strongly positively charged nature of the silicon moiety of the quartz matrix (Figure 12) [29].

Polyakov et al. [30] have shown the dependence of corona discharges during adsorption of oxygen and other gases on various metals, measuring the work functions of metal electrodes in relation to the nature of surface. Discharge potentials were found to be significantly lower in moist air than in dry air. In recent studies of mixtures of hydrocarbon gases with water, hydrogen bromide, and even hydrochlorofluorocarbons (normally considered as highly efficient flame extinguishing agents), it was discovered that instead of inhibiting ignition, these actually were ignition promoters [31, 32]! Thus, in further argument for an ionic rather than free radical pathway in initiation of hot surface ignitions, it can be noted that water, halons, and hydrogen

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* Dr. Lisa Pfefferle, Yale University, personal communication, 1992.

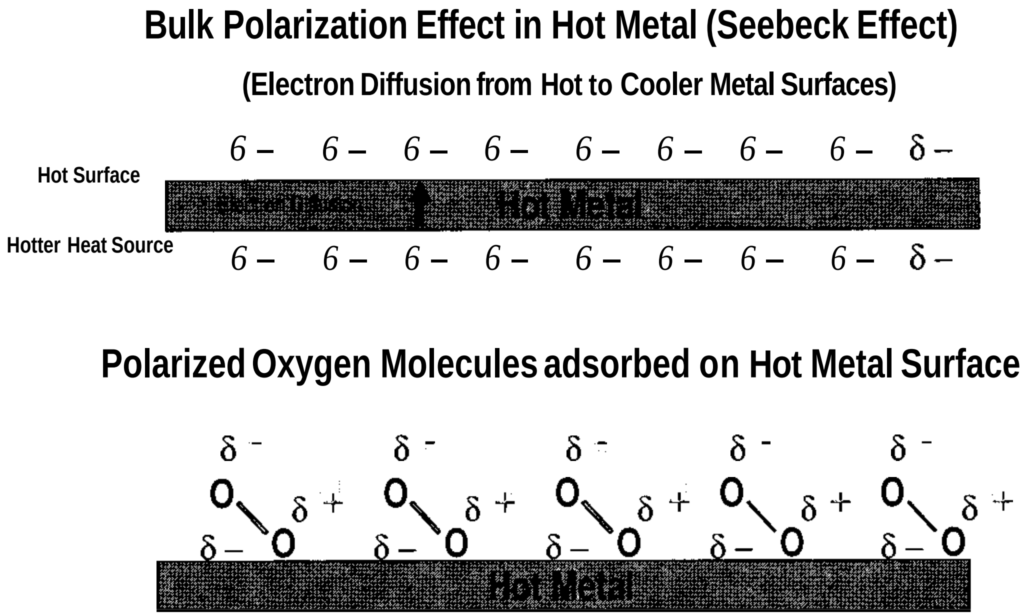

Figure I0. The Seebeck effect and resulting polarization of adsorbed oxygen on hot surfaces.

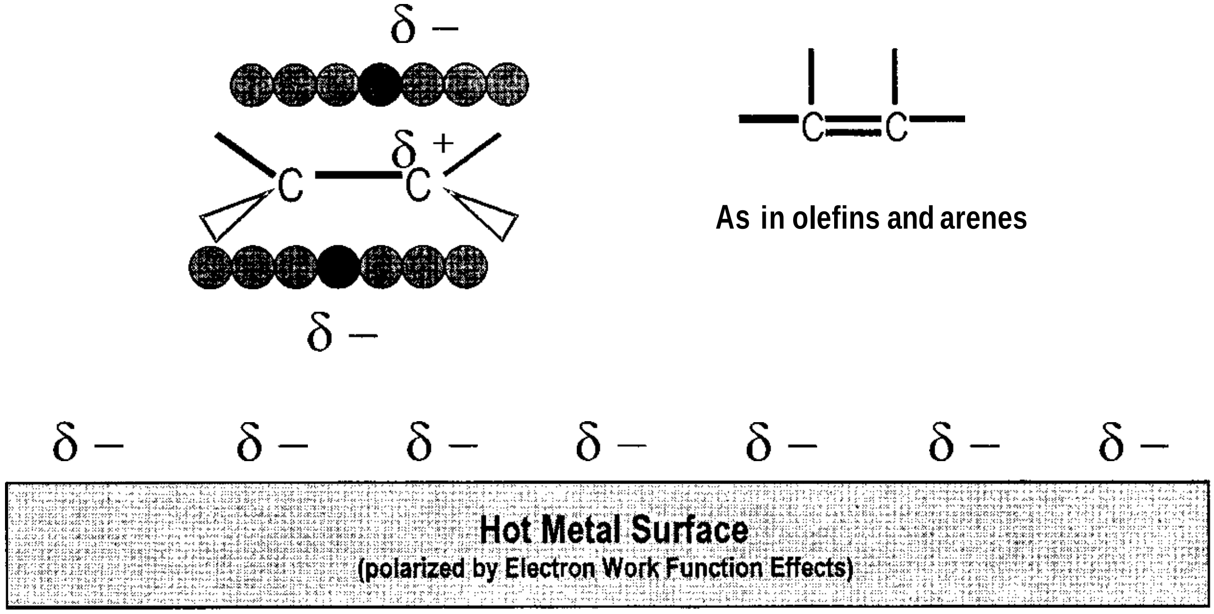

Figure 11. Anomalously high ignition temperatures of arenes and olefins, caused by repulsion of pi bonds by partially negatively charged hot surfaces.

Charge Densities due to
Electronegativies:

Silica surfaces have significantly
negatively charged surfaces/

Si 40% +
O 20% -

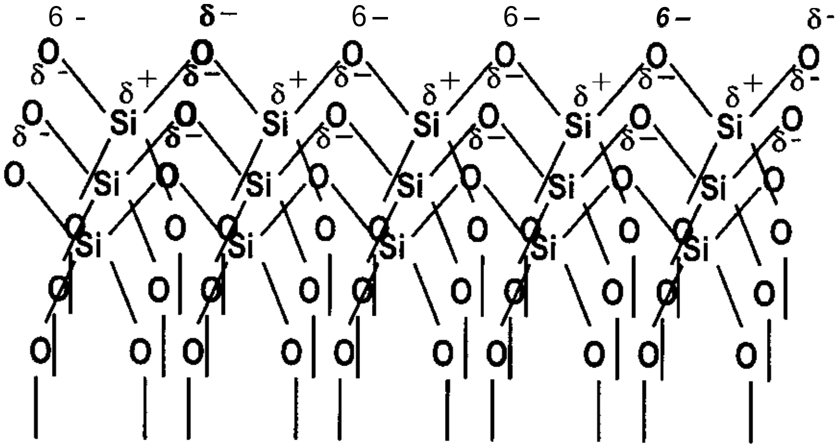

Figure 12. Polarization of quartz, glass and similar silica surfaces.

bromide are highly polar species, which would very appreciably polarize ambient air in the vicinity of the hot surface, thereby facilitating ionic ignition initiation processes.

Metal oxides have a profound attraction for adsorption of molecular oxygen, and molecular oxygen facilitates catalytic oxidations. Even if the metal surface is clean, there is a profound tendency for adsorption of atomic oxygen. Polarization of such adsorbed atomic species would result from the Seebeck effect, with partially negative charge character on these adsorbed oxygen atoms, thereby also providing a propensity for catalytic oxidations. Even with metals such as titanium, which does not significantly oxidize at normal temperatures, there is some degree of oxidation even at room temperatures. Moreover, when heated above 250 °C, as occurs when heat treating takes place to increase metal strength, very significant oxidation does occur [33, 34}.

Thus, existing evidence implicates thermal polarization of oxygen and fuel molecules (induced by polarizing effects of the hot surface), as shown in Figure 13. The high gas phase Bronsted basicity [11] of the negative dipole of the excited oxygen molecule on the hot surface can abstract a proton the thermally excited fuel molecule, forming an adsorbed carbonation/hydroperoxy cation pair, which then combine to form adsorbed alkyl peroxides. These then thermally dissociate to form initially adsorbed free radical species. When enough of these accumulate in a sufficient population, these can desorb and participate with energized fuel molecules in conventional cool and hot flame free radical propagations. Stabilizing or destabilizing influences in such free radical propagation systems would remain entirely operational from this stage on.

## FUTURE RESEARCH

1. Construction of a miniaturized hot surface temperature apparatus.

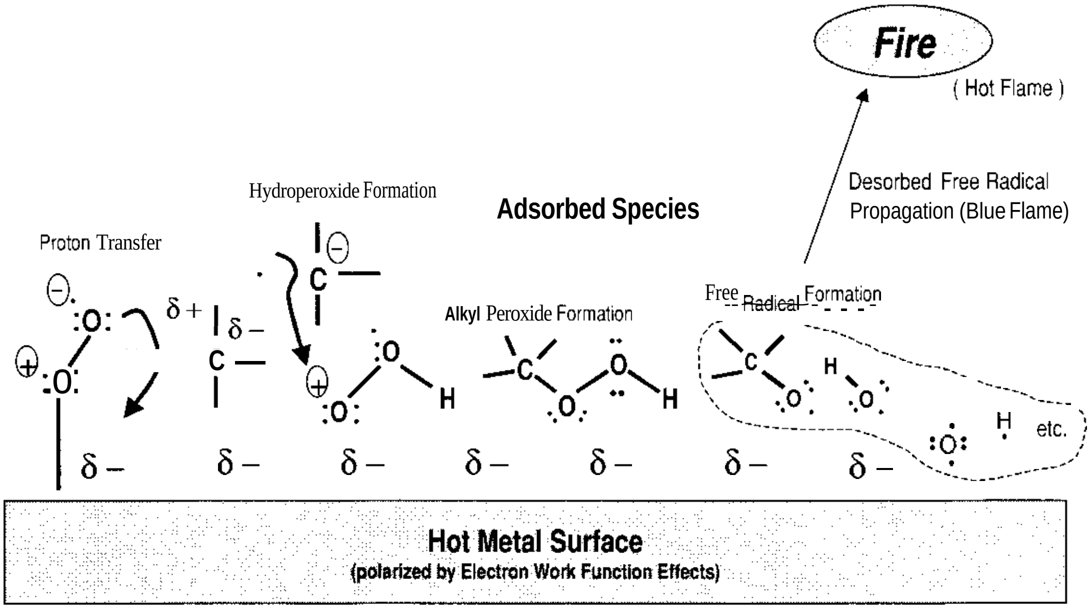

Figure 13. Ionic Effects in Hot Surface Ignition.

2. Use of infrared radiation or lasers to heat the hot surface. This should make the hot surface the hottest part of the heated body. to install a partial positive charge at this surface, and thus would be predicted to promote higher ignition temperatures.
3. Application of direct positive charges to the hot surface. (This could have implications in terms of prevention of fires on hot surfaces.)
4. Suggestions for use of isomerized, branched chain analogs of n-alkane (straight chain) jet fuels. These would have considerably higher ignition temperatures, with additional features such as lower viscosity and lower melting points (with favorable implications for high altitude refueling operations and for use in Arctic conditions.)
5. Isotope effect studies. with deuterated fuels. High isotope effects would indicate free radical pathways: low values would favor ionic mechanisms.
6. Investigation of cationic (positively charged), rather than anionic firefighting agents such as AFFF. Cationic agents may be useful in mitigating reignition or other ignition phenomenon.
7. Suggestions of use of metals or alloys with hot temperature ignition characteristics for hot surface ignition problem areas, as in aircraft engines and dry bays, or with low hot surface ignition characteristics for use in cold-start diesel engines.

## ACKNOWLEDGMENT

Initial support for this work was provided by the Air Force Office of Scientific Research and by the National Institute of Standards & Technology. The assistance of Kermit Smyth, Nelson Bryner and Steve Semancik (NIST); Richard Vickers, Douglas Dierdorf, Barry Mitchell, Douglas Nelson and J. Michael Bennett (Air Force Research Laboratories); Anthony Finnerty (US Army Research Laboratory); Professor Lisa Pfefferle (Yale University); and Arthur Watterson

(University of Massachusetts at Lowell) is gratefully acknowledged. This paper is dedicated to Joseph Walker, head of the former Fire Research Labs at Tyndall AFB, FL; and to Homer Carhart and Joseph Leonard, former heads of the Fire Research Lab at Naval Research Laboratories, Washington, DC, whose early support and constructive advice inspired the conception of this project.

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