ANIONIC EFFECTS IN HOT SURFACE COMBUSTIONS

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ABSTRACT

Hot surface oxidations are commonly thought to involve initial free radical hydrogen atom abstraction. Our evidence implicates initial Lewis base deprotonation by $O\bullet^{-}$ atomic oxygen radical anions to form negatively charged carbanions. Subsequent rate determining electron transfers generate free radicals which only then give rise to combustion. Correlations regarding ignition temperatures and hydrocarbon oxidation product identity are consistent with carbanionic but not free radical effects. Highly polarized surfaces (e.g., quartz and corroded surfaces), and addition of polar compounds to fuel/air mixtures facilitate ignitions. EFM confirms increased electrostatic intensities at microscopic surface defects. For seemingly uniformly hot surfaces there are transient widely disparate high temperature incandescent "red spot" zones due to flameless oxidations induced by concentrated electrostatic negative charges at surface defects. Isotope, ignition temperatures and combustion trends are consistent with Seebeck effects (ease of electron migration in unevenly heated areas). There are preliminary though not yet verified indications that electrostatic charges on hot surfaces may facilitate combustion. Implications would then involve fire mitigation and enhancement, and industrial manufacture of many important organic combustion products.

GENERAL

In selective (flameless) oxidations of hydrocarbons, C-H bonds rupture with insertion or addition of oxygen species to form combustion products. In total oxidation (with or without flame), the hydrocarbon is completely oxidized to CO_2 and water. [1] Fuel flammability indices include flash points (the minimum temperatures for liquid fuels to sustain sufficient vapor concentrations in air to produce ignition when an open flame is passed over the surface); and hot surface ignition, or autoignition temperature [AIT] (with no open flame for a surface in contact with a given fuel causing "self-sustained combustion".[2] Currently accepted hydrocarbon oxidation mechanisms involve free radical attack by oxygen species such as the atomic oxygen radical anion below) on C-H bonds, to yield propagating alkyl free radicals and hydroxide ion; see (Equation 1): [3, 4]

$$R-H+{}^{-}:\underset{\cdot\cdot}{\ddot{O}}\cdot \rightarrow R\cdot+{}^{-}:\underset{\cdot\cdot}{\ddot{O}}-H \tag{1}$$

AIT determinations are subject to the test method. In recent videotaped work [5] to compare previously cited [6] AIT values of 240^{o} C for JP4 jet fuel with that of the much less volatile JP8, the same AIT was observed for both fuels but at a much higher temperature (540 ± 20^{o} C). Several previously unidentified features were noted; see Figure 1. After application of fuel drops onto a hot stainless steel surface, a dark envelope expanded outward, with wisps of smoke. Red-hot incandescent spots moved rapidly over the surface outward from this dark patch, at heating temperatures as low as 380° C, although red incandescence of iron typically occurs above 525 °C. [7] These incandescent events can last many seconds before actual flame formation occurs. (Other workers have also observed pre-flame "red spots". [8,9] Blue "cool" flames were often observed at the outer edges of the red spots, with almost immediate transformation of these flickering blue flames to a sheet of white-hot flame over the entire test area. The following sequence of events is speculated:

1.The fuel drop vaporizes, cooling the immediate impact area of the hot surface. Fuel concentrations within the cloud are initially above the upper flammability limit. [10]

2.Within the fuel cloud there is initial flameless oxidization, forming CO, CO_2, and water and further reducing O_2 levels. Heating causes thermal eddies and convection currents, effecting isolated contiguous hotter and cooler surface areas. Within hotter areas oxidation rates are enhanced to the extent that there can be momentary attainment of an incandescent "red spot", flickering and moving around as a result of convection currents.

3. For "red spots" at the periphery of the fuel cloud, where oxygen levels are higher in contiguous cooler areas (but still hot enough to sustain ignition), the fuel/air mixture may be lean enough to afford ribbons of blue "cool flame" along this periphery, which suddenly transform to a sheet of white hot flame over the entire surface.

Other workers have shown that combustion occurs prior to flaming combustion, with CO and CO_2 being prominent products; see Table 1. [11]

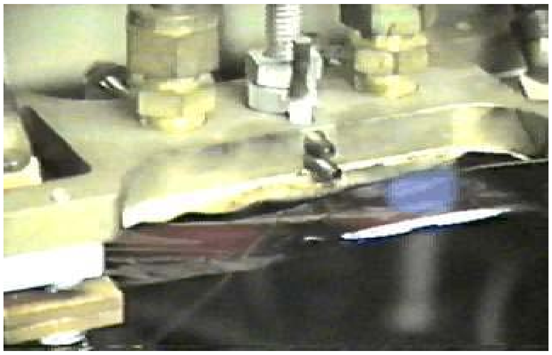
Table 1. Oxidation of 9 % CH_4/air at 1050 °C (about 500 °C below maximum IT).

Gas Present	With Pt^o bar, %	With Ni^o bar, %
Natural gas, at start	9.1	8.99
CO_2, after 8 minutes	1.01	0.05
CO, after 8 minutes	0.72	0.50
Natural gas, at start	8.75	8.77
CO_2, after 20 minutes	1.96	0.07
CO, after 20 minutes	0.22	0.36

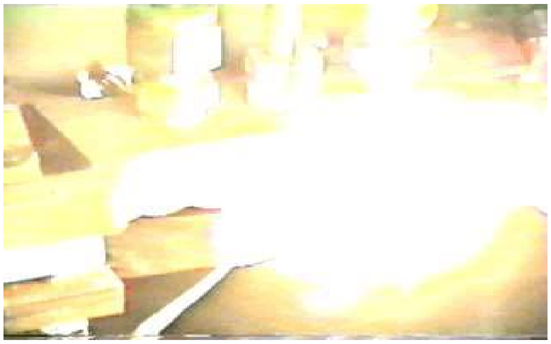
The observed AIT of 540 °C for both JP4 and JP8 can be attributed to CO formation, with an AIT somewhat higher (609 ° C). The transient incandescent red spots do not persist long enough for true temperature registration, but would be hot enough for CO ignition. Also, the range of lower to upper flammability limit [10] is much greater for carbon monoxide (12.5 % to 74 %, ideal for a fuel rich environment) than for alkane fuels (e.g., hexane, with very narrow ranges of 1.1 % to 7 % [2]. Thus, AIT determinations may pertain not to the substrate being measured, but rather to decomposition products such as carbon monoxide.

Figure 1. Hot Surface Precombustion, Flameless Combustion and Ignition: JP-4 on stainless steel surface at 380 °C.

Fuel droplet vaporizes on hot surface, at ca. 380 °C. Hemispherical fuel rich cloud of vapor expands outward, with some smoke. Low molecular weight decomposition products (CO, etc.) diffuse rapidly to periphery of fuel cloud. Decomposition raises local surface temperatures to over 520 °C, with incandescent red hot spots fleeting over the steel surface.



As surface temperatures increase to ca. 540 °C, blue "cool" flames flicker at outer periphery of red spots.



Sudden transformation of blue flame to "hot" flame over entire test area.

This suggests that the first pre-flame phase is a relatively low energy selective process. As will be discussed, we believe adsorbed oxygen radical anions thermally react as strong Lewis bases with the hydrocarbon C-H bonds to form carbanionic incipient intermediates. These then undergo electron transfer to form corresponding hydrocarbon free radicals, and proceed through previously documented mechanistic pathways to form selective and total oxidations products. As oxidation ensues with rising temperatures, the rate of formation of the free radical population also increases. When the rate of free radical propagation exceeds the rate of flameless free radical depopulation processes, runaway flame chemistry ensues.

GENERAL CONSIDERATIONS: ANIONIC VS. FREE RADICAL MECHANISMS

FUEL CHARACTERISTICS (see Figure 2):

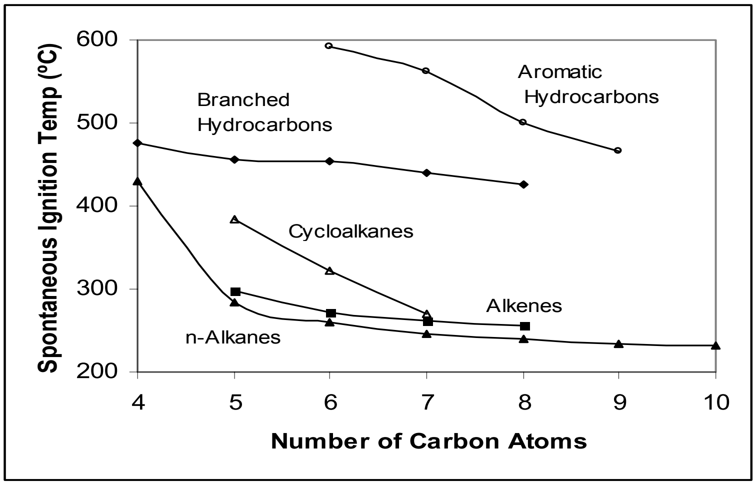


Figure 2. AIT values for various hydrocarbon families [10]. These trends in AIT values are exactly opposite to trends involving free radical reaction proclivities for these species. [12 – 15].

Fire reactions are commonly considered to be in the gas phase, and it is true that free radical (and positively charged cationic) reactions tend to proceed with much less energy reqirements than is the case for ionic reactions in the gas phase. [15] However, pre-flame combustion reactions take place by interaction with oxygen species adssorbed onto the solid phase surface of a hot target; and gas phase arguments are not applicable. For example, the gas phase free radical process is favored for the free radical reaction (2) over the ionic gas phase dissociation (3) of HCl [15] (both being highly endothermic reactions):

$$HCl \rightarrow H.Cl. \qquad \Delta D = 103 \text{ kcal/mole} \qquad (2)$$

$$HCl \rightarrow H^{+}Cl^{-} \qquad \Delta H_{f} = 186 \text{ kcal/mole} \qquad (3)$$

On the other hand, impingement of gaseous HCl onto a basic solid surface such as NaOH obviously results in an exothermic ionization process.

POLARITY IN AMBIENT AIR EFFECTS

In studies of mixtures of hydrocarbon gases with halons, hydrogen bromide, and water (all highly efficient polar fire extinguishing agents which appreciably polarize ambient air in the vicinity of hot surfaces), it was found that instead of inhibiting ignition, these actually were ignition promoters! [16,17] These results provide further argument for a polar rather than a free radical pathway in facilitating ionic ignition initiation processes in surface ignitions.

HOT SURFACE CHARACTERISTICS

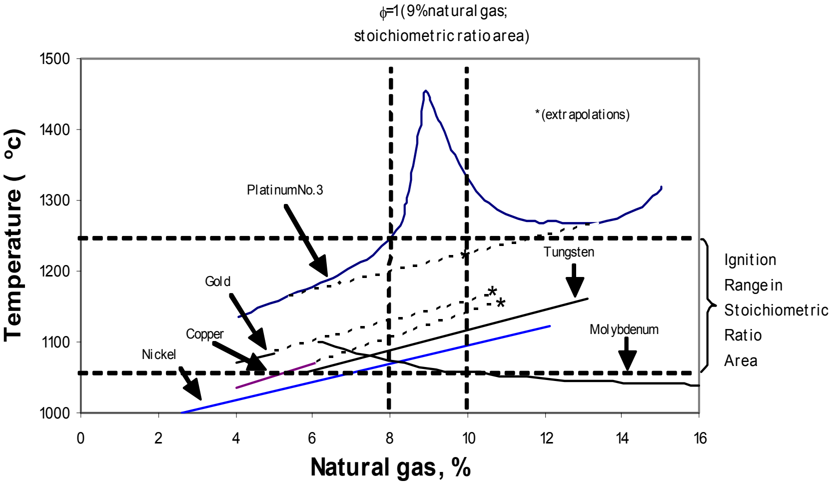


Figure 3. Natural gas ignition on hot metal surfaces, with considrable flameless combustion below AIT's. [11] "The sharp maximum in temperature for Pt^{o} is an artifact caused by transient surface heating as ignition occurs" [18]. (This is reminiscent of the "red spot" ignition described on pages 2-3 and in Figure 1.)

1. Seebeck Effects Favoring Polar Combustion Mechanisms

In heated metal surfaces with varying surface temperatures there are electrical charge effects with polarizing influences in these different zones. Seebeck effects induce charge transfers in heated metals, the polarity and magnitude of these depending on the metal. Many ("n-type") metals exhibit a negative Seebeck effect, with a diffusion of electron density toward the cooler side, and a corresponding partially negatively charged character at the cooler side. For positive "p-type" metals (such as tungsten, molybdenum, copper, gold and silver), there is a reversed electron diffusion from cooler to hotter metal surfaces, and a corresponding positively charged polarization at the cooler end.. [19-24] (See Figure 4.)

> **Note**: In the context of Figure 4, the "hot" end in the system is the driving heat source, and the "cool" end is the combustion surface on which the actual "hot surface combustion" takes place. Thus, as temperatures rise on the cooler surfaces during combustion for the "n-type" metals, this surface becomes *less* negatively charged as there is a relative migration of electron density back to the hotter end. It will be shown that combustion is dependent on negative charge character, and therefore combustion tendencies on such n-type metals will require hotter and hotter temperatures. Likewise, for the "p-type" metals the negative charge character at the combustion surface will *increase* during combustion, thus requiring lower temperatures for ignition to take place. Thus, "n-type" metals would be expected to have higher ignition temperature, and "p-type" metals would have lower ignition temperatures.

In confirmation of this principle, there is an inverse correlation of ignition temperatures in Figure 3 with the Seebeck values of these metals, as shown in Table 2. In the order shown, metals with the highest positive coefficients have lower ignition temperatures, and metals with higher negative values have higher ignition temperatures.

The "n-type" nickel species appears to be anomalous, in terms of its relatively low ignition temperature. However, the nickel surface (unlike all the other metals discussed here) becomes irreversibly oxidized at temperatures below typical AIT values. As discussed in the next section, metal oxide coatings provide lower ignition temperatures than do non-corroded metals.

Thus, relative potentials for oxidation are also included in Table 2. Melting points are provided to indicate that these are in the solid state for the typical AIT ranges (1170 K – 1270 K [900^{o} – 1000^{o} C]) for most fuels.

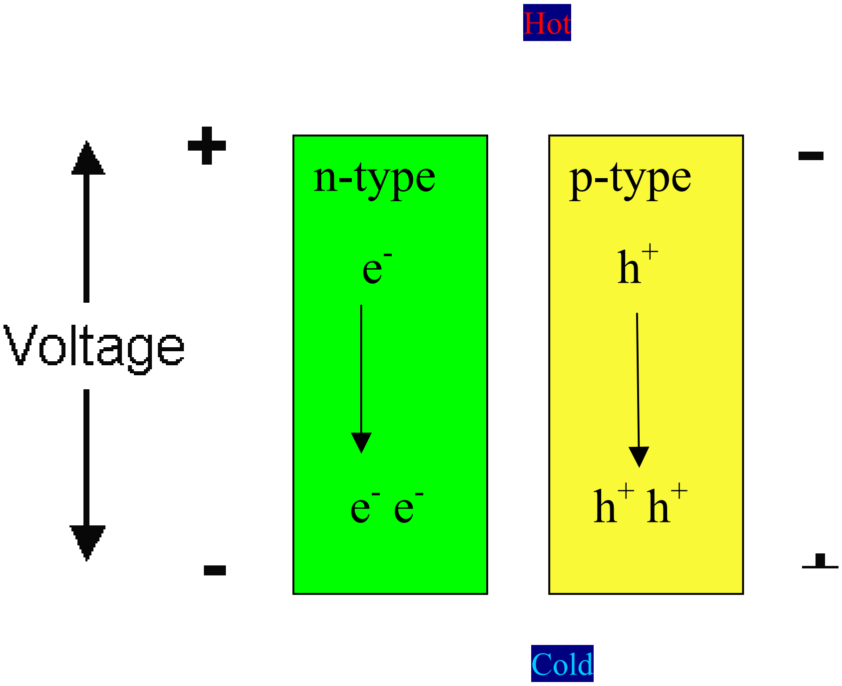


Figure 4. Polarization by Seebeck effect for negative n-type (e.g., Ti, Pt, Ni, and Pd) and positive p-type coefficient metals (e.g. W, Mo, Cu, Ag, Au). [24]

Table 2. Thermoelectric Power and Ignition Proclivity for Combustion Catalysts.

	Metal	Autoignition temp, ^{o}C (see Fig. 3)	Seebeck effect (μv/^{o}C), 1000^{o}C - 1300^{o}C) [19]	M.P. (^{o}C) [26]	Oxidation Comments [27]
P –type	W	1040 – 1110	17 to 19	3410	Stable to aerial oxidation.
	Mo	1080 – 1050	ca. 17	2617	”
	Ag	--	8 to 10	962	Oxidizes at lower temperatures; but oxide reverts to metal in AIT range.
	Cu	1100 – 1130	5.3	1083	”
	Stainless steel	--	3 to 4 [27]	1427	Stable to aerial oxidation
N - type	Au	1120 – 1180	-3 to 8	1064	”
	Ti		-5 to - 2	1650	”
	Pt	1200 – 1240	-18 to -21	1772	”
	Ni	1080 – 1100	-30 to -35	1453	Oxidizes at lower temperatures; oxide is stable in AIT range.
	Pd	--	-31 to -34	1552	Stable to aerial oxidation.

2. Oxyanionic and Corroded Surface Effects

As noted above, there is an apparent negative electrostatic character to be associated with facilitation of combustion. Although it is non-metallic with no Seebeck effect, and there are typically no significant surface defects (see discussion below), quartz is a highly efficient ignition source, with the lowest of all the ignition temperatures.[28] This may be due to the strong polarization of adsorbed oxygen molecules, due to the very high negative charge of the oxygen species which comprise the entire surface of the silicate matrix (see Figure 5).[19] Similar considerations can be made for other oxidized surfaces, such as nickel oxide and iron rust, also excellent ignition sources.[29,30,31] There have also been findings of "p-type" character of oxides of metals such as nickel, for which the metal itself possesses "n-type" character. This effect would serve also to reduce ignition temperatures. [32]

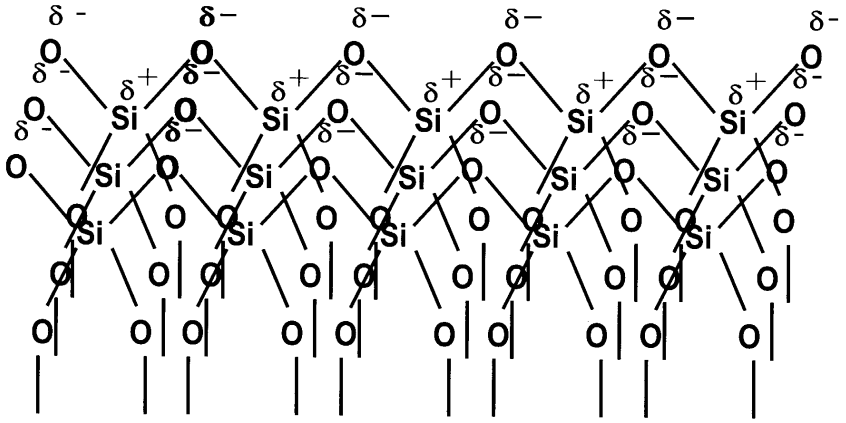


Figure 5. Polarization of quartz, glass and similar silica surfaces, with charge densities due to electronegativies: Si, 40% positive; O, 20% negative.[33]

3. Electrostatic Field Effects Arising from Surface Microdefects

The magnitude of Seebeck coefficient charge effects (typically microvolts/°C change in temperature) may appear to be very small, but microscopically all surfaces are entirely covered by considerable defects in terms of terraces, steps, ledges, and kinks and similar elevated features (see Figure 6). [29-31]

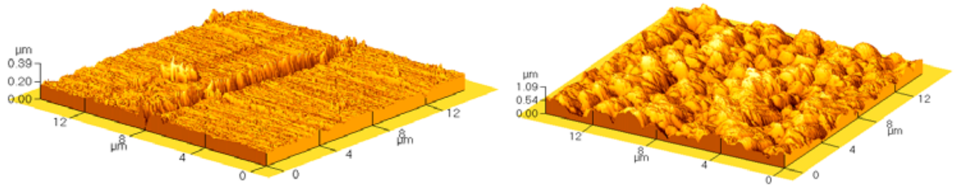


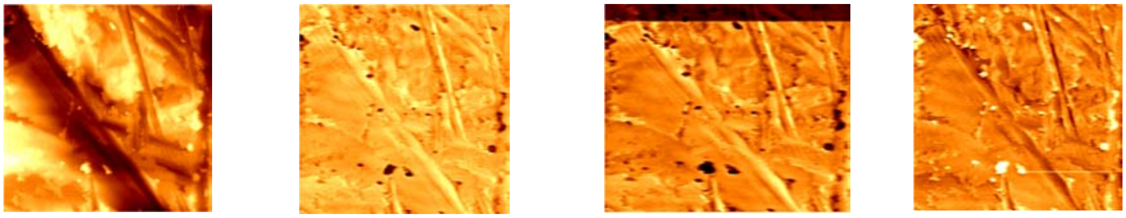
Figure 6. AFM images of polished sterling silver (left), and of the same sample (right) coated with a surface oxide film.

Increased catalytic activity and electrical effects at the tips or edges of such features have also been observed. [29,30] In this connection it can be noted that electrostatic field effects totally accumulate at the topmost tips of these types of surface features. Since the area comprising these tips is exceedingly miniscule in comparison to the total surface area, there is accordingly a very drastic increase in density of these localized charges. [34] An inference can then be drawn from this effect in terms of surface microdefects at a hot surface (with a hotter heat source driving a heat flow and Seebeck electron drift to or from this surface). On microscopic examination such surfaces exhibit an uneven landscape characterized by valleys with surrounding steppes, shelves, cliffs, spires and crags.

EXPERIMENTAL RESULTS

ATOMIC FORCE AND ELECTROSTATIC FORCE MICROSCOPY (AFM/EFM)

AFM examinations at surfaces exhibit an uneven landscape characterized by valleys with surrounding steppes, shelves, cliffs, spires and crags. Experiments were performed with electrostatic force microscopy (EFM) to show that polar effects in hot surface ignitions may be initiated at select pinpoint areas of the surface, where electrostatic effects are reintensified due to the localized micro surface defect character and localized energizing. EFM measures spatial variation of surface charge carriers at the microscopic level, mapping surface charges, dielectric constants and electrical potentials on surfaces, as can be generated by the Seebeck effect and the resulting polarization of adsorbed oxygen on hot surfaces.[35] Several metals (Ni, Mo, and Pt) were studied to measure relative surface potentials simultaneously with topography. The EFM was focused on effects of DC probe tip bias voltage changes toward difference of surface potentials at room temperature. (No temperature gradient was imposed; thus no Seebeck effects were involved.) In future work we intend to study such effects for a variety of positive and negative Seebeck effect systems, with large temperature gradients.) The AFM/EFM results for nickel for various imposed surface voltages are shown in Figures 7 a-d; similar results pertained for the other metals. The contrast of features in EFM is related to the electrostatic strength between the probe tip and sample. The AFM signal in each case reveals numerous promontories due to surface imperfections, at which electrostatic charge intensities are concentrated. With a positively charged probe tip and negatively charged sample, the attractive force between the unlike charges show up as brighter portions of the image, being concentrated at these surface peaks. The EFM voltage is relative to the strength of electrostatic interaction between the tip and the sample. Conversely, when both probe tip and sample are positively charged, repulsive forces between like charges show up as darker portions.



a. AFM topography. b.EFM, +5 volts c. EFM, 0 volts d. -5 volts

Figure 7. AFM and EFM views of polished nickel surface at various applied voltage levels. (Constant temperature, 25^{o} C; no Seebeck effect)

It can be reasoned that polar effects in hot surface ignitions are initiated at select pinpoint areas of the surface, wherein electrostatic effects are particularly exacerbated due to the localized micro surface defect character and localized energizing.

POSSIBLE NEGATIVE CHARGE ENHANCEMENT OF OXIDATION.

A combustion apparatus as illustrated in Figure 8 has been constructed. Preliminary, incomplete results indicate that hot surface oxidations are facilitated by application of negative electrostatic charges to the surface.

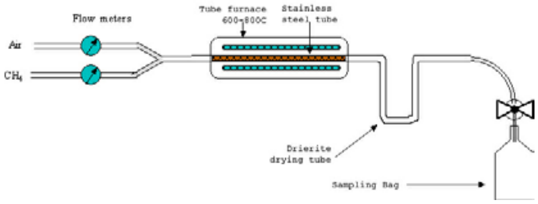


Figure 8. Combustion apparatus.

Preliminary results of oxidation of a fuel-rich mixture of methane and air in a stainless steel tube at 650 °C are shown in Figure 9.

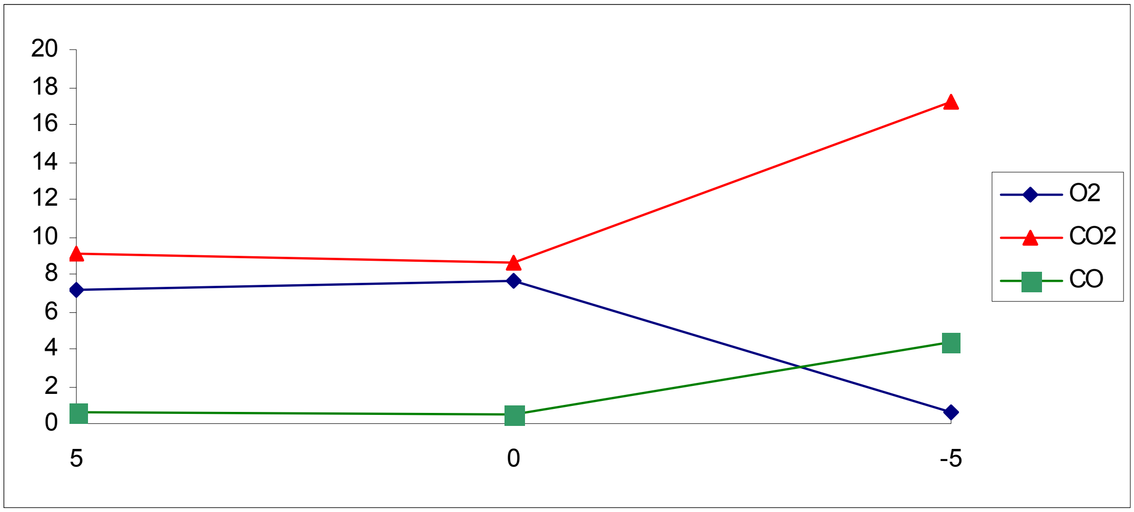


Figure 9. Percent combustion *vs.* kilovolt electrostatic surface charge. (Negative charges appear to enhance oxidation.)

PROPOSED CARBANIONIC RATHER THAN FREE RADICAL MECHANISM

A currently accepted mechanism [36,37,38] for hot surface hydrocarbon oxidations involves a preliminary attack in which a C-H bond is severed by an attacking highly reactive species such as a hot surface energized adsorbed atomic oxygen radical anion (see Figure 9), producing two fragments. In one of these the hydrogen is transferred to the attacking species; the other is the hydrocarbon radical (less the hydrogen) remaining after the C-H bond rupture; see equation (4).

$$:\ddot{\underset{..}{O}}\cdot^{\,-}$$

Fig. 9. Atomic oxygen radical anion. (The abbreviated notation is $O\bullet^-$)

$$R\text{--}H + O\bullet^- \rightarrow R\bullet^- + H\text{--}O^- \rightarrow \text{selective and/or total oxidation} \quad (4)$$

hydrocarbon Δ alkyl free hydroxide
radical anion

The atomic oxygen radical anion has three non-bonding electron pairs, and a seventh lone (free radical) electron. The three electron pairs impart strong Lewis basicity, in addition to its free radical character. In the commonly accepted theory, the $O\bullet^-$ radical anion attacks *via* its lone radical electron in a high energy rate determining reaction pathway to afford energetic propagating free radicals. These further engage in free radical propagations to yield a variety of selective oxidation products. Accompanying energy releases can result in flame oxidation.

Various kinetic isotope effect studies [36,37,38] have been cited as apparent substantiation of the free radical nature of these oxidations.

From evidence gathered by our group, the much lower energy initial step involves attack by the very highly basic $O\bullet^-$ radical anion, to form an alkyl carbanion and a hydroxyl free radical. A high energy rate determining electron transfer from the carbanion to the hydroxyl free radical then results in an alkyl free radical and hydroxide anion. The same products arise, but through a much lower energy ionic pathway before proceeding into a higher energy free radical mechanism (see Figure 10); and the same isotope effects apply for both free radical and ionic pathways.:

$$\text{R--H} + \text{O}\bullet^- \rightarrow \text{R:}^- + \text{H--O}\bullet \dashrightarrow \text{R}\bullet + \text{H--O}^- \qquad (5)$$

hydrocarbon alkyl carbanion hydroxyl free radical alkyl free radical hydroxide anion

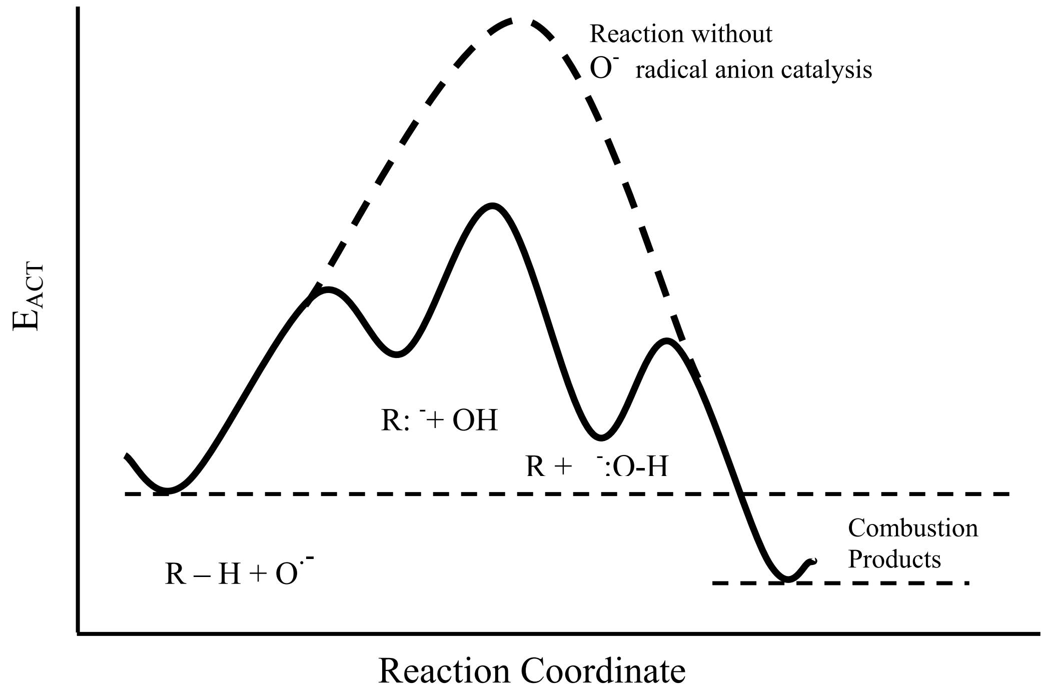


Figure 10. Reaction coordinate for $O\bullet^-$ catalyzed and uncatalyzed oxidations.

In the solvated state, hydrocarbon pK_A values are about 62, but when unsolvated and at elevated temperatures these are much stronger Bronsted acids with much lower pK_A values; and in the presence of a strong base such as the unsolvated atomic oxygen radical anion adsorbed on a hot surface, an acid/base interaction would be expected to occur. [4,39]

FUTURE INVESTIGATIONS

If it can be established that negative electrostatic charges do indeed facilitate combustion effects, and positive charges diminish combustion effects, a study of red spot development leading to cool "blue" and subsequent hot flame development may be useful in devising means of mitigating ignitions. Thus, an IR photometric sensing system could detect onset of heat buildup at potential preignition sites prior to red spot development, to trigger a discharge of positive character to the specific area. Likewise, a stream of gaseous inerting agent could be directed to the specific area, serving to lower oxygen concentrations out of the lower to upper level flammability limits; or possibly a rapid water deluge extinguishing system could be activated more quickly than might be achievable with a flame detection system.

There are strong implications in terms of extension of these principles to industrially important hydrocarbon oxidations. Thus, we intend to look at the conversion of methane to carbon monoxide (and other derivatives), of butane to maleic anhydride, and other important processes to determine if negative charge applications can facilitate these reactions.

ACKNOWLEDGMENTS

An early grant from NIST enabled the commencement of this research work. Support from the University of Massachusetts (Lowell) CFCI (Committee of Confederated Centers and Institutes) over the past four years for graduate research assistants is gratefully acknowledged. The following individuals and agencies have provided valuable advice and assistance throughout more than a decade of work on this project:

Tyndall AFB (FL) Fire Research Labs:
Richard Vickers, Dr. Douglas Dierdorf,
Barry Mitchell, Douglas Nelson and
Joseph Walker (ret.)

Nat'l Institute of Standards and
Technology: Drs. Kermit Smyth and
Richard Gann; Nelson Bryner.

USAF Research Labs (Dayton):.
Dr. J. Michael Bennett.

Univ. of New Mexico: Drs. Edward Walters;
Robert Tapscott, Douglas Mather (both ret.)

US Army Ballistic Research Labs: Dr.
Anthony Finnerty (ret.)

Yale University: Dr. Lisa Pfefferle

IMR Environmental Equipment Co.
(St. Petersburg, FL): Dr. Dieter Gromadzki

California Institute of Technology /JPL):
Dr. Jeff Snyder

University of Limerick (Ireland): Dr. B. K

U.S. Naval Research Labs: Drs. Homer
Carhart and Joseph Leonard (both retired)

Michigan State University: Dr. Tim Hogan;
Dr. Frank Blatt (ret.)

Hodnett

Arizona State University: Drs. Robert Peck, Thomas Korb

Univ. of Maryland: Drs. Jungho Kim and Ken Yu

Univ. of Massachusetts (Lowell): Drs. Arthur Watterson, James Whitten, Jun Li, John Hobbs, Changmo Sung

Lincoln University (Oxford, PA): Dr. Saligrama SubbaRao.

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