

Effect of Chemical Structure on Spontaneous Ignition of Hydrocarbons

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SPONTANEOUS ignition properties of combustible materials, particularly fuels and hydrocarbons, have been an important area of combustion research for over 50 years. This interest in spontaneous ignition is based on the important role which this phenomenon plays in the fire hazard in the handling and storage of combustibles, the performance of various types of combustion engines, and the elucidation of oxidation and combustion mechanisms of fuels, hydrocarbons, and related substances.

The spontaneous ignition temperature (SIT) of a substance is defined as that lowest temperature at which the substance will ignite in air without the aid of a spark or flame. Based on the thermal theory of ignition and on classical reaction-rate theory, spontaneous ignition temperature can be regarded as that temperature to which a combustible mixture must be raised so that the rate of heat evolved by the exothermic oxidation reactions of the system will just overbalance the rate at which heat is lost to the surroundings. However, the criterion that is usually taken to indicate ignition—i.e., visible and/or audible combustion observed under ordinary laboratory conditions—is quite subjective. Also, the spontaneous ignition temperature of a substance should be a quantity related to some characteristic chemical property of the material, yet its experimentally determined value is markedly dependent on the method and apparatus employed for its determination. In a recent monograph, Mullins (17) reviews this subject, including the importance, definition, and meaning of spontaneous ignition and spontaneous ignition temperature and describes numerous methods for its determination and the factors which influence results.

Earlier work on the effects of oxygen concentration (2, 12–14) indicated that it would be of interest to study spontaneous ignition in finer detail using better instrumentation with particular emphasis on preignition behavior. A static system was chosen for its simplicity and to make temperature-time measurements. An inherent fault of such a system is the problem of uniform gas mixing after introducing the hydrocarbon sample. This problem should be minimized by discharging the sample as a fine spray and by a long time delay before ignition occurs.

The general purpose of this investigation was to study the influence of chemical structure on the spontaneous ignition processes. Specifically, the influence of chain length, chain branching, unsaturation, and of cyclic and aromatic structures on the preignition processes was examined by measuring internal gas temperature and oxygen consumption.

In addition to minimum ignition temperature in air for cool- or hot-flame ignition, minimum reaction temperature, preignition temperature range, temperature rise, and oxygen consumption at ignition were useful. A correlation between these values and ease of oxidation and ignition was noted. The findings were as follows:

In general, decreasing chain length, addition of methyl groups, unsaturation, and particularly, chain branching increased oxidation and ignition resistance of aliphatic hydrocarbons, as was indicated by higher values for

minimum ignition and minimum reaction temperatures, temperature rise, and oxygen consumption at ignition. Preignition temperature ranges for highly branched paraffins were about six to seven times that of straight-chain compounds. The ranges for the five branched hydrocarbons investigated had similar values, and the gas temperatures just before ignition were all approximately the same (445° C.). This suggests that perhaps these hydrocarbons pyrolyze to fragments which behave similarly in the oxidation processes.

Alicyclic compounds were more resistant to oxidation than the analogous straight-chain compounds, and the aromatic compounds were the most resistant of all compounds studied. Side chains decreased oxidation resistance for both cyclic and aromatic hydrocarbons and this effect increased with chain length. The cycloparaffins were unique in having exceptionally short preignition temperature ranges and exceptionally long ignition delays. Cyclopentane, however, was an exception to these generalizations, and its ignition characteristics differed markedly from that of the other cyclic compounds investigated.

Minimum reaction temperatures from this investigation for aliphatic hydrocarbons showed good correlation with both the experimental reaction rate data and the theoretical methyl retardation factors of Hinshelwood. Thus, the results of the present work agree with his views concerning molecular structure and resistance to oxidation as well as point of oxygen attack.

APPARATUS

The apparatus (Research Appliance Co., Box 307, Allison Park, Pa.) used by Setchkin (19) at the National Bureau of Standards for the determination of spontaneous ignition temperatures of combustible liquids was adapted for this work. It consisted of a 1-liter spherical borosilicate glass flask inside a refractory casing. The neck, top, and bottom of the flask are each heated by separate heater coils controlled individually and manually by auto-transformers. Temperature measurements are made by thermocouples located at each heater coil, the top and bottom of the flask, and one inside the flask. A temperature controller was added which made it possible to maintain uniform temperature within $\pm 1^\circ$ C.

A fine Chromel-Alumel thermocouple (28 B. and S. gage) connected to a fast-response recorder is used for measuring gas temperatures. It was necessary to use well-grounded shielding on the power cord, thermocouple leads, and the other wires leading into the recorder to eliminate external electrical interferences. All thermocouples were calibrated against a standard Pt-Pt-Rh thermocouple.

METHOD

After temperature adjustment had been made, the desired quantity, usually 0.2 ml. of hydrocarbon, was injected into the flask by means of a hypodermic syringe fitted with a 6-inch, 26-gage needle, and stopwatch time was recorded. The lights were extinguished. Then the inside of the flask was observed in total darkness through a 1/2-inch hole in the flask stopper with the aid of a mirror, while the temperature-time variations were being recorded. The time

and type of ignition was noted, along with any other pertinent observations.

Thus far, all work has been done in air at atmospheric pressure. The effect of variation in size of sample on ignition temperature is discussed by Setchkin (19) and Frank, Blackham, and Swarts (8) and in the work previously cited (12). Variation in sample size was also investigated. In certain instances, doubling the sample (0.4 ml.) may result in cool flames instead of hot flames, and decreasing the sample to about half or less at minimum ignition temperature may result in nonignition. In all work done thus far, small variations in sample size did not influence minimum ignition temperature values more than the experimental error of about 1° C., provided that no distinction was made between cool- and hot-flame ignition. Therefore, for uniformity, and to save time, a standard sample of 0.2 ml. was used. This sample represents approximately three to four times the stoichiometric quantity for most of the hydrocarbons investigated at their minimum ignition temperatures.

The problem of uniform gas mixing was minimized by injecting the sample as a fine spray. To test the extent of hydrocarbon-air mixing, several runs were made at the same temperature using the same hydrocarbon, but varying the vertical position of the thermocouple within the flask. No apparent difference in results was noted.

In the initial stages of this investigation, a fresh clean flask was used for each run. At temperature close to the spontaneous ignition temperature, erratic and nonreproducible results were obtained. By "conditioning" a flask with repeated use, this difficulty was overcome. The same flask therefore was used throughout.

To obtain additional information regarding the processes of ignition being studied, gas samples were taken for oxygen analysis after the reactions were completed. The oxygen concentration immediately after the charge was vaporized, but prior to oxidation, was calculated from the perfect gas law. Oxygen was determined after ignition by means of a Pauling magnetic susceptibility oxygen meter on 100-ml. samples obtained from inside the flask with a large hypodermic syringe fitted with a fine tube. After the gas sample was taken for oxygen determination, the gases in the flask were blown out with compressed air for about 2 minutes. Then, after temperature adjustment, the apparatus was ready for the next run.

The hydrocarbons studied were Phillips Petroleum Co. 99 mole % purity and each was purified further by percolation through silica gel and alumina.

TYPES OF IGNITION OBSERVATIONS

At least four different types of observations were noted (Table I), depending on the fuel and on the base temperature. Typical temperature-time ignition curves super-

Table I. Types of Ignition Observations

Classification	Observation	Temperature Rise
Negative	None	None
Preignition non-luminous reaction	None	Gradual
Cool-flame ignition	Faint silent bluish glow ^a	Sudden
Hot-flame ignition	Faint silent yellowish glow ^a to yellow, orange, and blue flames ^b	Sudden

^a Visible only in total darkness. ^b Intensity and audibility, weak "pop" to intense explosion, often with smoke, sometimes enough to mask substantial flames unless observed in total darkness.

imposed in a single diagram are illustrated for 2,3-dimethylbutane (Figure 1). In the figure exact magnitudes and positions are not intended to be necessarily significant as these curves have been sketched for illustrative purposes only. The initial dip in each curve is caused by cooling due to vaporization of the sample. Curve 1 is negative; curves 2 to 9 are preignition, nonluminous reactions; curve 10 represents a cool-flame ignition and curve 11, a hot-flame ignition. Although in this example the hot flame shows a greater temperature increase than the cool flame, this was not always the case, owing to inertia of thermocouple response.

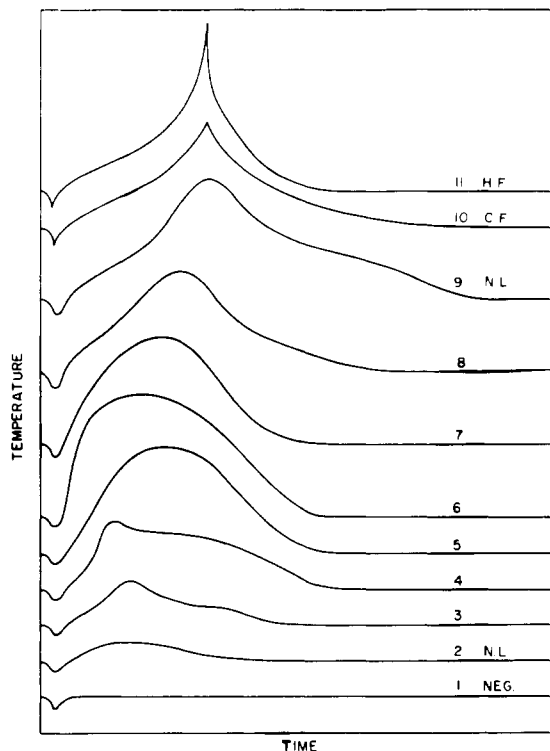


Figure 1. Typical ignition curves for 2,3-dimethylbutane in air

Curves sketched for illustrative purposes only

In the present study, rather than attempting to distinguish between the minimum hot-flame ignition temperature (SIT) and cool-flame ignition temperature, either cool flame or hot flame was accepted as representing positive ignition, and the criterion for ignition used was the sharp temperature rise noted on the recorder chart. An example of a recording at the minimum ignition temperature for *n*-hexane is shown in Figure 2.

RESULTS

Preignition curves for a representative hydrocarbon showing temperature rise and oxygen consumption *vs.* base temperature are shown in Figure 3. An unusual behavior, that of cyclohexane, is shown in Figure 4. Data for a variety of hydrocarbons are summarized according to structure in Tables II to V. The term "base temperature" refers to the initial temperature of the flask just prior to introduction of the fuel sample

T_i is the minimum reaction temperature, or the lowest base temperature at which a measurable temperature rise, ΔT , is observed. In general T_i also corresponds to the lowest temperature at which measurable oxygen consumption $\Delta \theta$ is noted.

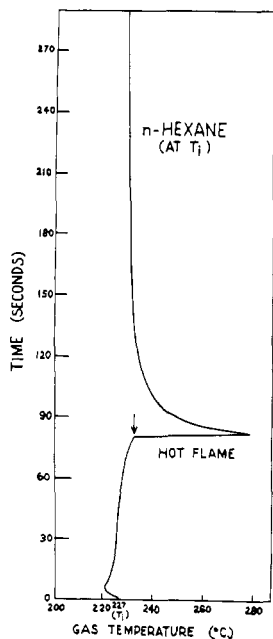


Figure 2. Temperature-time ignition curve for *n*-hexane in air at T_i

T_i is the minimum base temperature for cool- or hot-flame ignition.

$(T_i - T_r)$ is the preignition or nonluminous reaction zone.

ΔT is the temperature rise above the base temperature.
 $\Delta \theta$ is the oxygen consumption.

$\Delta \theta_s$ and ΔT_s represent the values obtained by extrapolation to T_i of a plot of $\Delta \theta$ and ΔT values respectively, vs. base temperature in the preignition zone. For example, for 2,2-dimethylbutane (Figure 3), the upper and lower curves intersect T_i (405° C.) at 74% oxygen consumption, and 38° C., the values reported for $\Delta \theta_s$ and ΔT_s , respectively.

$T_s = T_i + \Delta T_s$. Thus, T_s represents the gas temperature at incipient ignition or just before ignition occurs. The relative magnitudes of T_r , T_i , and T_s for the normal paraffins are shown in Figure 5. T_r , T_i , ΔT_s , and T_s are not unique physical quantities but are, in part, related to the geometry of the particular system used.

t_i is the ignition delay in seconds at T_i .

DISCUSSION

Straight-Chain Hydrocarbons. Ignition temperature, T_i , decreases with chain length (Table II), (1, 20, 24). T_r and T_s follow the same general trend, as shown in Figure 5. The meaning given to T_s is that it is the actual gas temperature at which ignition begins in distinction to T_i , which represents the starting base temperature.

ΔT_s and per cent $\Delta \theta_s$ both rise with chain length, as is shown in Figure 6. The ratio of the number of moles of oxygen consumed to the total number of moles of CH_2 groups in the flask is a constant value of 0.2 for the straight-chain paraffins. This value is obtained by dividing the oxygen-hydrocarbon ratio in Table II by the number of methylene groups in the molecule. Thus oxygen consumption appears to be a function of a number of methylenes rather than a molecular relation. This may suggest that the extent of oxidation increases as the number of CH_2 groups goes up, increasing the number of probable points of oxygen attack in the hydrocarbon molecule.

The preignition range ($T_i - T_r$) is relatively short, averaging about 22° C. Unsaturation appears to increase

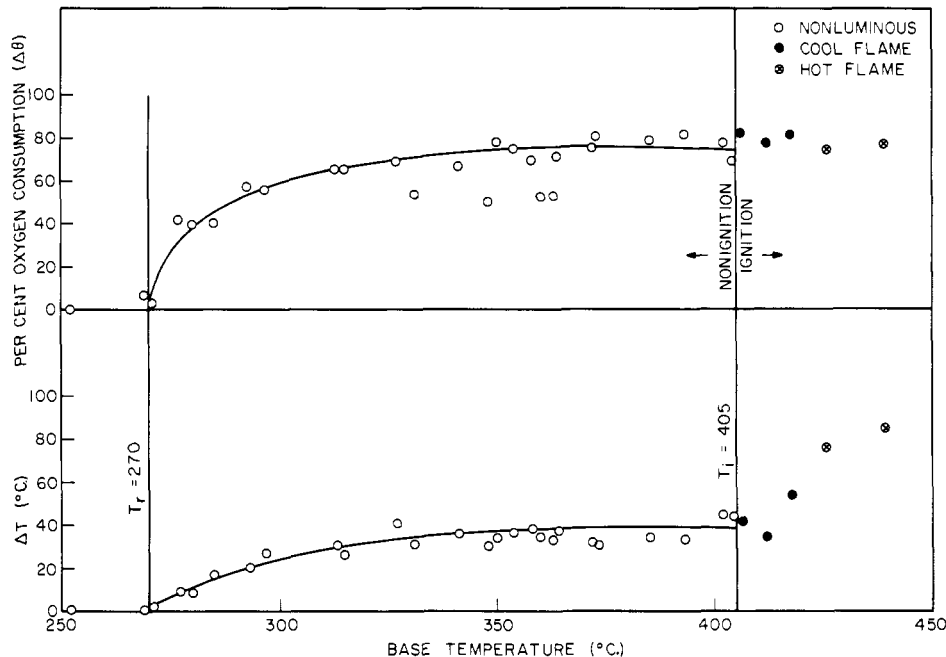


Figure 3. Temperature rise and oxygen consumption vs. base temperature in preignition zones for 2,2-dimethylbutane in air

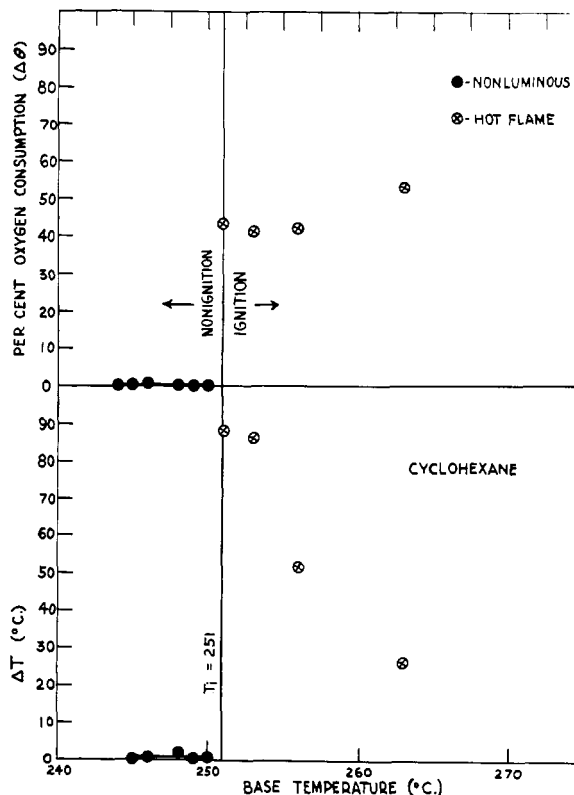


Figure 4. Temperature rise and oxygen consumption vs. base temperature in preignition zones for cyclohexane in air

resistance to oxidation in the straight-chain hydrocarbons investigated, as is demonstrated by the rise in T_i , T_s , and (except for 2-hexane) T_r . This is also in accordance with the findings of other investigators of ignition phenomena (13, 20, 22).

The normal hydrocarbons, particularly *n*-octane, *n*-nonane, and *n*-decane, in certain of the preignition runs

Table II. Summary of Preignition Data for Straight-Chain Hydrocarbons

Hydrocarbon	Temp., ° C.					Oxygen Consumption		
	T_r	T_i	T_s	$(T_i - T_r)$	ΔT_s	$\Delta\theta_s$, %	Mole ratio, O_2 /hydrocarbon	t_i , Sec.
<i>n</i> -Hexane	206	227	236	21	9	23	0.8	76
<i>n</i> -Heptane	195	213	224	18	11	25	1.0	102
<i>n</i> -Octane	184	206	218	22	12	27	1.2	112
<i>n</i> -Nonane	180	205	217	25	13	30	1.5	116
<i>n</i> -Decane	179	201	216	22	15	32	1.7	144
1-Hexene	217	253	264	36	11	63	1.9	57
2-Hexene	203	245	259	42	14	65	2.0	187
1-Octene	208	230	240	22	10	30	1.2	96

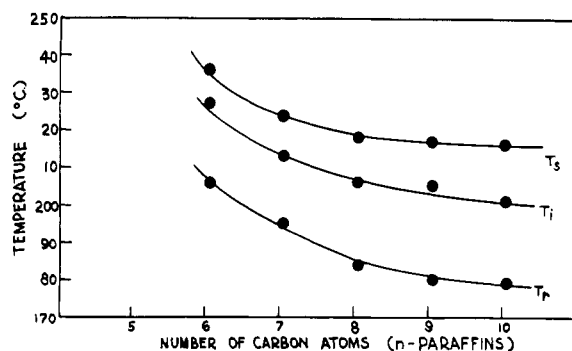
showed a temperature-drop (4° to 5° C.) followed by a temperature rise in the early stages of their reactions. These drops occurred after temperature recovery following vaporization. This is consistent with the findings of Salooja (18), who attributed these endothermic reactions to formation of hydroperoxide radicals.

Hexane Isomers. A wider spread of structural differences is shown for six-carbon hydrocarbons in Table III. The hexane isomers are listed in the usually accepted order of increasing resistance to oxidation (11, 22) and appear to fall into two groups. The data in Table III more or less follow this same order within the two groups. In general, the more easily oxidized group, including *n*-hexane and the two methylpentanes, has lower T_r and T_i values and much shorter preignition ranges ($T_i - T_r$) than the two dimethylbutanes, which are more difficult to oxidize. The ranges of the two highly branched hexane isomers are about five to seven times as long as those of the other three isomers. Also apparent is the shift to higher temperatures with increased branching and resistance to oxidation.

The single methyl group appears to increase oxidation resistance as indicated by a rise in T_i , as well as in T_r and T_s . One double bond appears to have a somewhat similar type of influence, which is in accord with the theories of Ubbelohde (22). However, neither the double bond nor the single methyl group exercises as much influence on the oxidation as does the pronounced effect of higher branching.

The higher ΔT_s and oxygen consumption for the dimethylbutanes can probably be explained as due to the greater extent of the oxidation reactions at higher temperatures.

Branched-Chain Hydrocarbons. Because of the marked effect of branching on the ignition temperatures which were observed in the hexane isomers, it was decided to investigate this phenomenon further. Shown in Table IV are five highly branched paraffins (including the two

Figure 5. Relation of number of carbon atoms to T_r , T_i , and T_s for *n*-paraffins in air

dimethylbutanes mentioned), and an unsaturated branched hydrocarbon. The influence of branching is again demonstrated in high oxidation resistance as shown by high values for T_r , T_i , and T_s , and particularly the long ($T_i - T_r$) range.

The saturated hydrocarbons in Table IV all have approximately the same value for T_s , averaging about 445° C. Also, ($T_i - T_r$) ranges for all of the branched hydrocarbons investigated have nearly similar values (the one exception being 2,3-dimethylbutane, which is somewhat lower). This similarity might be explained by pyrolysis (perhaps oxygen-induced) of these hydrocarbons to fragments which behave similarly in the oxidation processes.

In 2,4,4-trimethyl-1-pentene, the single unsaturated branched compound investigated, a decrease in T_r and T_i agrees with the views of Hawthorne and Scott (10) that in highly branched hydrocarbons unsaturation decreases resistance to oxidation. However, ($T_i - T_r$) is the same as that of its analogous saturated compound, iso-octane

Table III. Summary of Preignition Data for Hexane Isomers and Other Six-Carbon Hydrocarbons

Hydrocarbon	Temp., ° C.					Oxygen Consumption		
	T_r	T_i	T_s	$(T_i - T_r)$	ΔT_s	$\Delta\theta_s$, %	Mole ratio, O_2 /hydrocarbon	t_i , Sec.
<i>n</i> -Hexane	206	227	236	21	9	23	0.8	76
2-Methylpentane	233	264	275	31	11	52	1.6	31
3-Methylpentane	259	278	305	19	27	65	1.9	27
2,2-Dimethylbutane	270	405	443	135	38	74	1.8	18
2,3-Dimethylbutane	278	396	446	118	50	82	2.0	58
1-Hexene	217	253	264	36	11	63	1.9	57
2-Hexene	203	245	259	42	14	65	2.0	187
Cyclohexane	250	251	258 ^a	1	9 ^a	°	°	525
Methylcyclopentane	246	258	266 ^a	12	8 ^a	°	°	400
Benzene	474	548	583	74	35	72	0.9	74

^a Because of short preignition range, it was not possible to determine ΔT_s and $\Delta\theta_s$ from preignition data. $\Delta T_s'$ and T_s' were obtained from ignition data.

(2,2,4-trimethylpentane). The contribution of branching to the ignition properties of 2,4,4-trimethyl-1-pentene, far outweighs that of its double bond. This concept was mentioned also in the discussion of the hexane isomers.

All of the highly branched paraffins gave the characteristic bulging temperature-time traces resembling that of 2,3-dimethylbutane, which is shown in Figure 1.

Cycloparaffins. The cycloparaffin hydrocarbons proved to be one of the most interesting groups whose ignition properties were investigated, and in general this group was in a class by itself. Data for the cycloparaffin compounds are given in Table V. As a rule these compounds (cyclopentane was an exception) were characterized by very short ($T_i - T_r$) ranges and very long ignition delays (t_i).

Cyclohexane, for example, had a ($T_i - T_r$) range of about 1° C. or less, and its t_i was almost 9 minutes. Setchkin (19) also found long ignition delays for cyclohexane and methylcyclohexane. The extremely short ($T_i - T_r$) range is shown in Figure 4. The temperature scale in Figure 4 is deliberately magnified beyond the usual experimental accuracy and control of about 1° C. No measurable temperature rise nor oxygen consumption was found as near as 1° below T_i . A special run was made at 250° C, and a gas sample was taken for oxygen analysis about

1 minute before ignition was anticipated. The sample revealed no measurable oxygen consumption, which indicated that no apparent oxidation had taken place up to that moment. It was curious to note that the ignition in the flask took place on time, even though the gas sample had been withdrawn.

The addition of side chains to the cyclic ring decreased the resistance to oxidation, as was indicated by lower T values. This and the fact that the cycloparaffin compounds were more resistant to oxidation than the analogous normal paraffins were in agreement with the findings of others (10, 13, 20). Side chains caused an increase in the ($T_i - T_r$) range. The single unsaturated cyclic compound investigated, cyclohexene, had slightly lower T_r and T_i values than that of cyclohexane, but its ($T_i - T_r$) range was the same.

Methylcyclopentane had the same general characteristics as the other alicyclics, but cyclopentane behaved entirely differently. This T_i value was about 100° C. higher than that of methylcyclopentane, its ($T_i - T_r$) range was long, and its ignition delay time relatively short. The general shapes of the time-temperature recorder traces for cyclopentane were more like that of the highly branched compounds (such as in Figure 1 for 2,3-dimethylbutane) than that of the other alicyclics which resembled the straight-chain hydrocarbons for which Figure 2 is typical.

Because of the extremely short preignition range (Figure 4), it was not feasible to obtain ΔT_s and $\Delta \theta_s$ values for the cyclic compounds (except cyclopentane) from the preignition data. However, a value for ΔT_s could be approximated using data in the positive ignition region. If one examines the temperature-time ignition curve for n -hexane, a point of "incipient ignition" is noted as shown by the arrow in Figure 2. The gas temperature had risen from the base temperature to this point just before ignition occurred. This is the meaning of T_s , as stated under the straight-chain hydrocarbon discussion. If we call the temperature rise from the starting base temperature to the point indicated by the arrow, $\Delta T_s'$, we obtain a value T_s' as follows:

$$T_s' = T_i + \Delta T_s'$$

If it can be shown that at the minimum ignition temperature $T_s = T_s'$, then ΔT_s values for the cyclic compounds could be obtained from ignition data.

It was decided to test this idea with compounds for which both ΔT_s and $\Delta T_s'$ values could be obtained. This could be done with the straight-chain compounds and with the two methylpentane isomers. The highly branched compounds, cyclopentane, and the aromatic hydrocarbons exhibited time-temperature curves which were too gradual, and points of incipient ignition could not be obtained by this technique. As a generalization, it would appear that this point of incipient ignition can be detected in compounds in the so called "low-temperature" oxidation range (below about 300° C.), but not in those which ignite by the "high-temperature" (above about 400° C.) hydrocarbon oxidation mechanisms. This arbitrary classification is used throughout the combustion literature (6, 20).

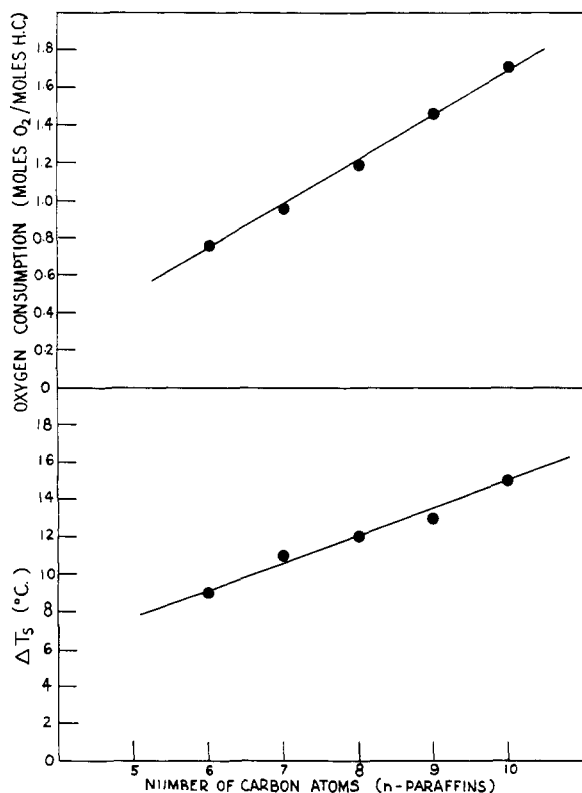


Figure 6. Relation of number of carbons to ΔT_s and to oxygen consumption for n -paraffins in air

Table IV. Summary of Preignition Data for Branched-Chain Hydrocarbons

Hydrocarbon	Temp., ° C.					Oxygen Consumption		
	T_r	T_i	T_s	$(T_i - T_r)$	ΔT_s	$\Delta \theta_s$	Mole ratio, O ₂ /Hydrocarbon	t_i , Sec.
2,2-Dimethylbutane	270	405	443	135	38	74	1.8	18
2,3-Dimethylbutane	278	396	446	118	50	82	2.0	58
2,2,3-Trimethylbutane	265	412	447	147	35	76	2.0	87
2,2,4-Trimethylbutane	263	407	443	144	36	75	2.3	50
2,2,3-Trimethylpentane	261	396	432	135	36	70	2.1	94
2,4,4-Trimethyl-1-pentene	234	377	416	143	39	64	2.0	22

Table V. Summary of Preignition Data for Cycloparaffin and Aromatic Hydrocarbons

Hydrocarbon	Temperature, °C.					Oxygen Consumption		
	T_r	T_i	T_s	$(T_i - T_r)$	ΔT_s	$\Delta\theta_s, \%$	Mole ratio, $O_2/\text{Hydrocarbon}$	t_i , Sec.
Cyclopentane	276	361	416	85	55	56	1.0	42
Methylcyclopentane	246	258	266 ^a	12	8 ^a	"	"	400
Cyclohexane	250	251	258 ^a	1	9 ^a	"	"	525
Methylcyclohexane	234	239	248 ^a	5	8 ^a	"	"	550
Ethylcyclohexane	227	238	250	11	13 ^a	67	2.3	450
Cyclohexene	243	244	252 ^a	1	8 ^a	"	"	762
Benzene	474	548	583	74	35	72	0.9	74
Toluene	440	532	553	92	21	57	0.7	39
Ethylbenzene	383	436	451	53	15	54	1.1	20

^a Because of the short preignition range, it was not possible to determine ΔT_s and $\Delta\theta_s$ from preignition data. $\Delta T_s'$ and T_i' values were obtained from ignition data.

A plot of ΔT and $\Delta T'$ values against base temperature is shown in Figure 7 for *n*-hexane. The curves in Figure 7 appear to intersect at a common value at T_i . Rather than obtain $\Delta T_s'$ values from a single point by measuring $\Delta T_s'$ at T_i on the temperature-time chart, a plot of $\Delta T'$ vs. base temperature was made and the curve extrapolated to T_i (Figure 7). The point of the intersection of the curve

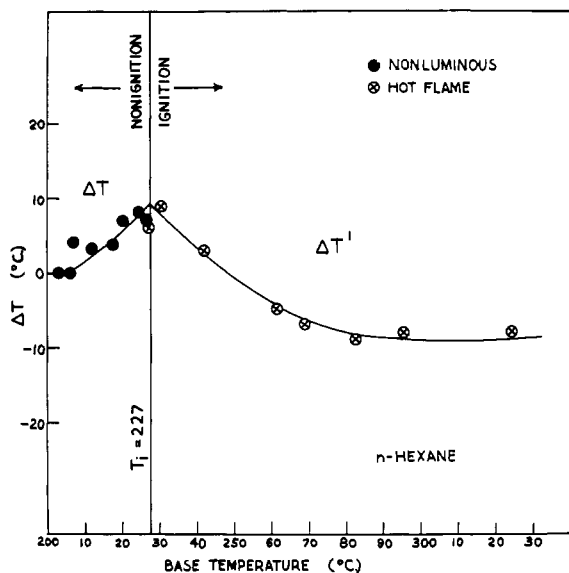


Figure 7. Comparison of temperature rise vs. base temperature in preignition zone with temperature rise at incipient ignition in ignition zone for *n*-hexane in air

with T_i was then accepted as the value of $\Delta T_s'$. This method was tried on the 11 applicable hydrocarbons, and in eight of these compounds, ΔT was equal to $\Delta T'$ at T_i , or in other words, $\Delta T_s = \Delta T_s'$. However, $\Delta T_s'$ values were about 50% lower than ΔT_s for *n*-decane, 1-hexene, and 3-methylpentane. The 11 compounds tried included ethylcyclohexane, a cyclic, for which ΔT_s could also be determined approximately from preignition data.

The $\Delta T'$ values were plotted against base temperature for the cyclics, and the $\Delta T_s'$ values so obtained are reported in Table IV. The $\Delta T_s'$ values for the cycloparaffins are lower than those of most of the other hydrocarbons investigated.

Aromatic Hydrocarbons. The data for the three aromatics investigated are shown in Table V. The aromatics exhibited

the highest ignition temperatures of all the compounds studied, and were clearly the most resistant to oxidation. This is in accord with the literature (9, 10, 20). As with the cyclics, side chains appear to lower the resistance to oxidation, the effect increasing with larger chains. This also is as expected (10). The aromatics exhibited a moderately large $(T_i - T_r)$ range, and the temperature-time recorder traces were, as previously stated, of the same general type as that of the highly branched hydrocarbons.

Hydrocarbon Oxidation in the Gas Phase. An enormous amount of work has been done in the investigation of gas phase hydrocarbon oxidation, and many methods have been employed. Numerous mechanisms have been proposed to explain the formation of the many reaction products which have been detected in oxidation reactions (6, 11, 21, 23).

The course which the oxidation reactions will follow will depend on the nature of the peroxides produced from the hydrocarbon. Thermal stability of a peroxide depends on its structure, which in turn is dependent on the structure of the original hydrocarbon, RH, and on the point of oxygen attack in the hydrocarbon. The point of oxygen attack is determined by the structure of RH.

The thermal stability properties of peroxides (16) can be generalized that primary peroxides are very unstable, whereas secondary and tertiary peroxides are increasingly more stable. This generalization is important in explaining the relative stabilities of straight-chain and branched hydrocarbons.

The point of initial oxygen attack is much discussed in the literature (15, 21, 23) of hydrocarbon oxidation, and it is generally agreed that this occurs at a tertiary carbon in preference to a secondary and finally to a primary. The point of "effective" oxygen attack, however, involves the combined questions of point of initial attack, and the matter of peroxide stability as well. Cullis, Hinshelwood, and their colleagues (3, 5, 11) conclude that in many cases, attack on the secondary carbon is of greater effect and importance than attack on the tertiary. This is because the peroxides formed by oxygen attack of the tertiary carbons yield relatively stable alkyl peroxides and other stable products such as ketones, whereas attack on secondary carbons yields less stable products which then proceed to further oxidation.

Relative oxidation rates of hydrocarbons at temperatures below ignition obtained by Cullis, Hinshelwood, and Mulcahy (5) are compared with T_r data in Figure 8. These data suggest a correlation between ease of oxidation and T_r . The relative oxidation rates were also determined under preignition conditions and are therefore comparable to T_r . It is interesting to note the transition (point of inflection) in the curve between the "low temperature" straight-chain

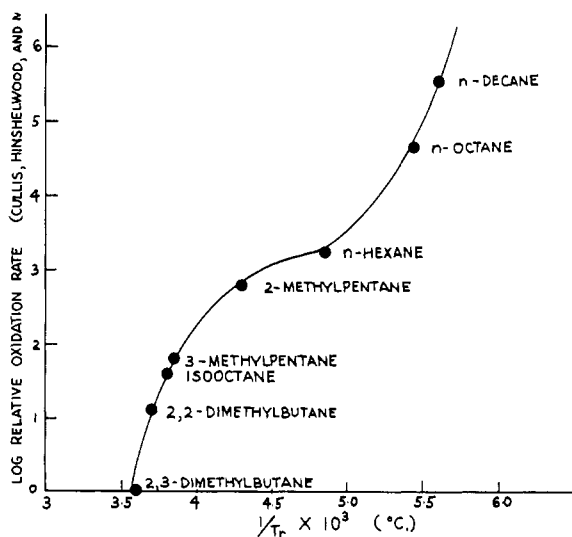


Figure 8. Comparison of Cullis, Hinshelwood, and Mulcahy oxidation rate (5) with T_r for paraffins in air

hydrocarbons, and the "high temperature" branched paraffins.

Hinshelwood's methyl retardation factor (11), recently called the "stability factor" by Cullis (3), can be used to determine the point of attack in the oxidation of saturated aliphatic hydrocarbons. In Figure 9, methyl retardation factor values are compared with T_r . The relationship shown (only triptane does not fall on the curve) implies that the T_r values found in this work are directly related to the point of "effective" oxygen attack, at least for saturated aliphatics.

The investigations of the ignition and oxidation properties of the cycloparaffins (1, 20) have shown that, as in the case of the aliphatic hydrocarbons, low temperature and high temperature oxidation mechanisms exist. The only literature reference found which set cyclopentane apart from the other cycloparaffin hydrocarbons was that of Tipper (21), who reported an unusually large amount of carbon dioxide in the oxidation of cyclopentane at 400° C.

No explanation is offered as to why the behavior of cyclopentane was so different from the other cycloparaffins which were investigated, nor why that of methylcyclopentane was not.

LITERATURE CITED

- (1) Allen, D.H., Carner, F.H., Long, R., Todd, J.R., *Combustion and Flame* **3**, 75 (1959).
- (2) Crellin, J.W., Johnson, J.E., Carhart, H.W., "Relation of Minimum Ignition Point to Other Ignition Phenomena," Division of Petroleum Chemistry, 125th Meeting, ACS Kansas City, Mo., 1954.
- (3) Cullis, C.F., *Petroleum (London)* **21**, 49 (1958).
- (4) Cullis, C.F., Hinshelwood, C.N., *Discussions Faraday Soc.* No. **2**, 117 (1947).
- (5) Cullis, C.F., Hinshelwood, C.N., Mulcahy, M.F.R., *Proc. Roy. Soc. (London)* **196A**, 160 (1949).

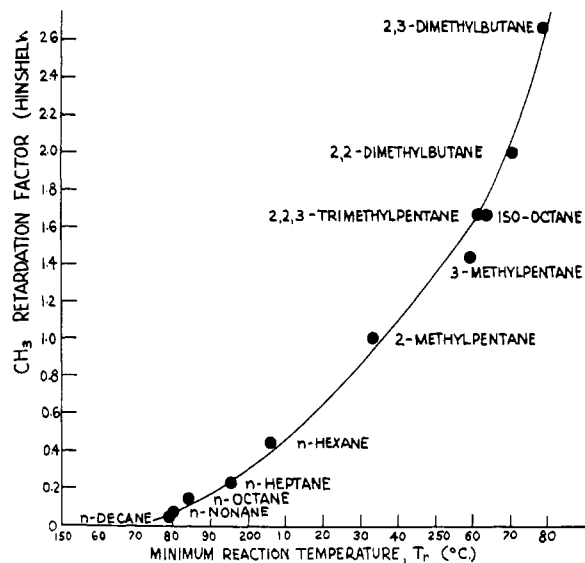


Figure 9. Comparison of Hinshelwood's methyl retardation factor (11) with T_r for paraffins in air

- (6) De La Mare, H.E., Vaughan, W.E., *J. Chem. Educ.* **34**, 64 (1957).
- (7) Frank, C.E., Blackham, A.U., Natl. Aeronaut. and Space Admin. Tech. Note **2549** (January 1952).
- (8) Frank, C.E., Blackham, A.U., Swarts, D.E., *Ind. Eng. Chem.* **45**, 1753 (1953).
- (9) Gibbons, L.C., Barnett, H.C., Gerstein, M., *Ibid.*, **46**, 2150 (1954).
- (10) Hawthorne, W.P., Scott, E.J.Y., *Advances in Chem. Ser.* No. **20**, 187 (1958).
- (11) Hinshelwood, C.N., *J. Chem. Soc.* 1948 p. 531.
- (12) Johnson, J.E., Crellin, J.W., Carhart, H.W., *Ind. Eng. Chem.* **44**, 1612 (1952).
- (13) *Ibid.*, **45**, 1749 (1953).
- (14) *Ibid.*, **46**, 1512 (1954).
- (15) Lewis, B., von Elbe, G., "Combustion, Flames, and Explosions of Gases," Academic Press, New York, 1951.
- (16) Milas, N.A., Surgenor, D.M., *J. Am. Chem. Soc.* **68**, 205 (1946).
- (17) Mullins, B.P., "Spontaneous Ignition of Liquid Fuels," AGARD Publications, London, 1955.
- (18) Salooja, E.C., *Nature* **183**, 602 (1959).
- (19) Setchkin, N.P., *J. Research Natl. Bur. Standards* **53**, 49 (1954).
- (20) Swarts, D.E., Orchin, M., *Ind. Eng. Chem.* **49**, 432 (1957).
- (21) Tipper, C.F.H., *Quart. Rev. London* **11**, 313 (1957).
- (22) Ubbelohde, A.R., "Six Lectures on the Basic Combustion Process," p. 53. Ethyl Corp. Detroit, 1954.
- (23) Walsh, A.D., *Trans. Faraday Soc.* **42**, 269 (1946); **43**, 297, 305 (1947).
- (24) Zabetakis, M.G., Furno, A.L., Jones, G.W., *Ind. Eng. Chem.* **46**, 2173 (1954).

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