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Precombustion Reactions and Knock

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PRECOMBUSTION reactions of hydrocarbons and their knocking tendencies in internal-combustion engines are little understood. Even less is known about the chemical interactions of mixtures of hydrocarbons that lead to the octane number of gasoline. A fundamental knowledge of these reactions could aid in manufacturing more economically the high-octane gasolines.

Ever since the discovery that individual hydrocarbons differ in tendency to knock (*22, 25*), the study of precombustion reactions of hydrocarbons has attracted many investigators. The results of these studies have been adequately reviewed recently (*16, 24*). Many attempts to correlate the engine performance of a wide variety of hydrocarbons with the precombustion properties have met with only partial success. Ignition temperatures, ignition delays, products and total heat of precombustion reactions, positions of cool flames in a tube, and other properties correlate poorly with knocking tendency. A general correlation has not been obtained, probably because either too limited an experimental method was used or knock was not regarded as a composite effect of all precombustion reactions. Only recently has an attempt been made to explain the knocking tendency of hydrocarbons in terms of several characteristics determined under comparable experimental conditions (*27*).

The fuel-air mixture in an engine goes through the entire temperature range of precombustion reactions. Knock occurs when the mixture autoignites before it is engulfed by the flame initiated by the spark (*31*). All types of reactions from initiation of hydrocarbon oxidation through cool-flame reactions to autoignition must take part in producing knock. Furthermore, the importance of these reactions ought to depend on the nature of the hydrocarbons and on the engine conditions.

The importance of various precombustion reactions to the knocking tendency of representative hydrocarbons was studied and areas were defined for further research. The simple, heated-crucible method (*11*) was used, and the reactions were followed by the temperature change in the reacting gas mixture. Several *n*-paraffins, isoparaffins, cycloparaffins, olefins, aromatics, and blends of aromatics in iso-octane were studied. Results were compared with the performance of the hydrocarbons in internal-combustion engines.

EXPERIMENTAL

All aliphatic hydrocarbons (Phillips) were specified to have a minimum purity of 99 mole %; the iso-octane and *n*-heptane were of ASTM grade. All were further purified by percolation through silica gel and Al_2O_3 before use. The aromatics (Mathieson) were percolated through Al_2O_3 before use. The blends were made from freshly percolated hydrocarbons. Cylinder oxygen was used without further purification.

A modified Moore apparatus (Figure 1) was used. It consisted of a stainless-steel block containing a 25-ml. combustion chamber, a shallow vaporization pan at the bottom, and two ducts that carried metered oxygen to the bottom of the combustion chamber. The block was placed in an electrically heated furnace, and the temperature was controlled within 2° C. by a thermocouple embedded close to the chamber wall. A second thermocouple suspended 1 cm. above the bottom of the chamber sensed the temperature changes occurring in the gas phase during precombustion reactions and activated a recorder with a full-range sweep of 0.5 second.

After the oxygen flow was adjusted to 1.3 ml. per minute for aliphatic hydrocarbons and to 13.5 ml. per minute for aromatics and blends, the temperature of the block was raised rapidly to about 200° C. A drop of fuel—about 0.01 ml.—was dropped into the vaporization pan, and the temperature variation in the gas phase was recorded. Then the chamber was purged with air, and the procedure was repeated at intervals of a few degrees until ignition. Induction periods were measured with a stopwatch. Maximum temperature changes at any temperature could be reproduced within 10%; ignition temperatures, within 3° C. The octane numbers of the hydrocarbons were taken from API data (*3*). Octane ratings of the blends were determined by the ASTM Research method.

BEHAVIOR OF HYDROCARBONS AND BLENDS

A typical plot of temperature changes (*11*) at various block temperatures is shown in Figure 2 for iso-octane. The curve joining the points is called a "thermal profile." A well-defined thermal profile exhibits three distinct reactions zones: cool flame (I), negative temperature coefficient (II), and autoignition (III). The highly exothermic cool-flame reactions appear at temperature T_i and reach maximum at T_m. Beyond this temperature, their intensity decreases until autoignition reactions take over and autoignition occurs at T_a.

The thermal profile is identical in shape with curves obtained by plotting rate of hydrocarbon consumption against temperature (*2*). It thus offers a means of rapidly scanning the reactivity of hydrocarbons toward oxygen over a broad temperature range. Furthermore, the characteristic temperatures and the maximum changes measure relative reactivity over the corresponding temperature ranges. They were used to compare the ease of oxidation of hydrocarbons of various classes.

***n*-Paraffins.** The thermal profiles of four *n*-paraffins, C_5 through C_8, are shown in Figure 3. The information obtained from these thermal profiles agrees well with the literature: lengthening of the CH_2 chain lowers T_i (*10, 15*), increases cool-flame intensity and hence reactivity toward oxygen (*13, 23*), and lowers T_a (*10, 16*). The two maxima in the *n*-hexane curve have also been reported previously (*18*).

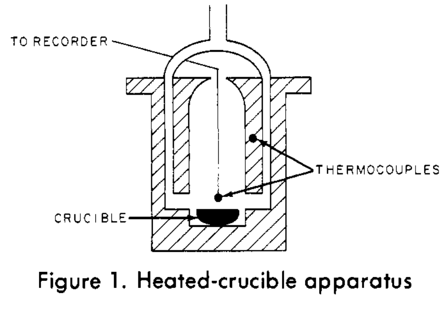

Figure 1. Heated-crucible apparatus

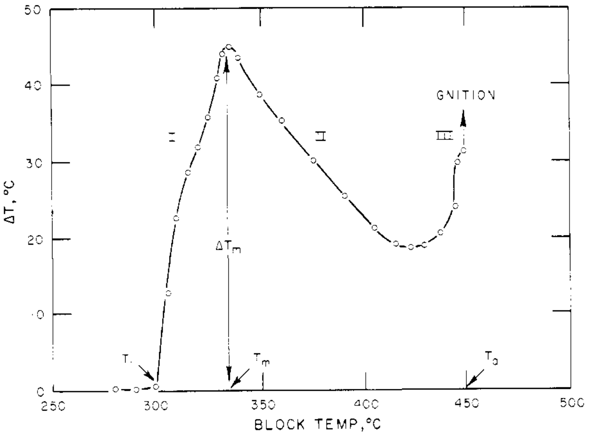

Figure 2. Thermal profile of iso-octane

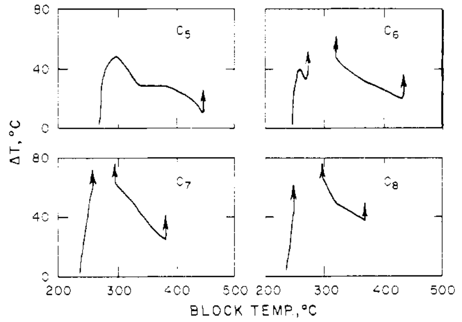

Figure 3. Thermal profiles of *n*-paraffins

The knocking resistance of these hydrocarbons qualitatively correlates with T_i, T_m, and T_a:

Hydrocarbon	Research Octane No.	T_i, ° C.	T_m, ° C.	ΔT_m, ° C.	T_a, ° C.
Pentane	62	263	300	50	442
Hexane	25	246	275	Ignition	428
Heptane	0	232	260	Ignition	388
Octane	−18	230	245	Ignition	367

No comparison can be made between octane numbers and ΔT_m, because only pentane has a well-defined cool-flame peak; the cool-flame reactions of the others are intense enough to ignite the mixtures. However, the octane numbers are in line with the temperatures at which autoignition occurs.

Isoparaffins. Branching, in general, decreases the ease of oxidation of hydrocarbons, as shown by the thermal profiles of isomeric hexanes in Figure 4. Furthermore, as the branching becomes symmetrical, the relative ease of oxidation decreases in the cool-flame region (*7, 13*). In the autoignition region, *n*-hexane closely resembles methylpentanes (*12*). Unlike *n*-paraffins, the autoignition temperatures of the isohexanes are not in the order of the cool-flame intensities; the unusual resistance of 2,2-dimethylbutane as compared with 2,3-dimethylbutane is noteworthy.

The order of the octane numbers of these hydrocarbons agrees well with the order of the maximum cool-flame intensities, with the temperatures at which exothermic reactions appear at maximum intensity, but not with the order of autoignition temperatures:

Hydrocarbon	Research Octane No.	T_i, ° C.	T_m, ° C.	ΔT_m, ° C.	T_a, ° C.
n-Hexane	25	246	275	Ignition	428
2-Methylpentane	73.4	274	300	50	434
3-Methylpentane	74.5	282	300	47	432
2,2-Dimethylbutane	91.8	296	317	32	490
2,3-Dimethylbutane	104	298	330	24	457

The unusual resistance of 2,2-dimethyl to autoignition reactions may explain its negative sensitivity. A hydrocarbon with greater resistance to autoignition should have lower octane depreciation upon going from Research to Motor conditions, where the hydrocarbon-oxygen mixture is subjected mainly to the higher-temperature region. Thus, the sensitivities of 2,2-dimethyl- and 2,3-dimethylbutane, −1.6 and 9.7, are inversely related to their autoignition temperatures.

Cycloparaffins. The thermal profiles of cyclopentane, cyclohexane, and their monomethyl derivatives are shown in Figure 5. Cyclopentane is the most stable of the group (*21*), and it alone exhibits a well-defined peak in the cool-flame region. The cool-flame reactions of the others generate enough heat to ignite the reaction mixtures. Nevertheless, the order of reactivity determined by the characteristic temperatures agrees well with published data (*1, 7*). A methyl group on the ring increases the reactivity; whereas this effect is small in cyclohexane over the entire temperature range, it is pronounced in cyclopentane in the cool-flame and autoignition regions. The explanation for this difference must await further experimentation.

The octane numbers for this group are in the order of the temperatures at appearance of exothermic reactions and autoignition:

Hydrocarbon	Research Octane No.	T_i, ° C.	T_a, ° C.
Methylcyclohexane	74.8	279	379
Cyclohexane	83.0	284	384
Methylcyclopentane	91.3	293	408
Cyclopentane	102	295	445

Although no correlation is possible with cool-flame intensities because of ignition, the ignition temperatures are also in the expected order.

Olefins. The thermal profiles of 1- and 2-hexenes, 2 methyl-1-pentene, 4-methyl-2-pentene, and cyclohexene are reproduced in Figure 6. Unsaturation generally increases the resistance of hydrocarbons to oxidation in the low temperature region (*4, 5*), as shown by the higher temperatures at which exothermic reactions appear. The reverse effect of some hydrocarbons beyond the cool-flame region is evidenced by the absence of regions of negative temperature coefficient and autoignition for hexenes and 4-methyl-2-pentene, in contrast to their saturated analogs. Furthermore, as the double bond is moved toward the center of the chain, reactivity decreases in straight-chain hexenes (*20*), but the effect appears again to be reversed in methylpentenes. The experimental conditions may be responsible for the almost identical value of T_i for the olefins studied (*1*).

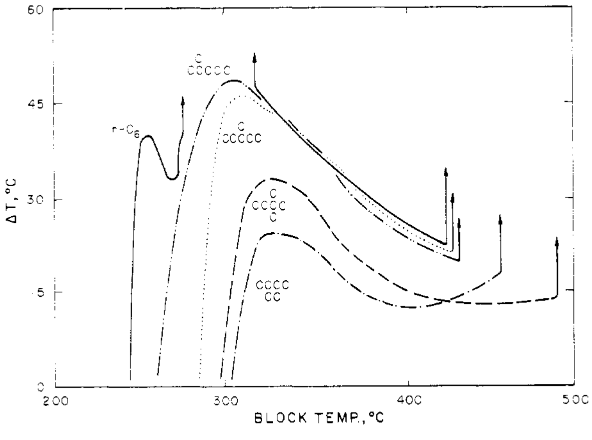

Figure 4. Thermal profiles of isomeric hexanes

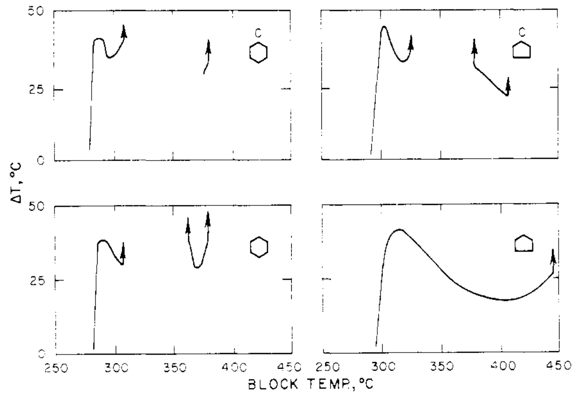

Figure 5. Thermal profiles of cycloparaffins

The knocking tendencies of these olefins agree well with their precombustion properties:

Hydrocarbon	Research Octane No.	T_m, ° C.	ΔT_m, ° C.	T_a, ° C.
1-Hexene	76.4	285	Ignition	...
2-Hexene	92.7	302	Ignition	...
2-Methyl-1-pentene	94.2	325	44	350
4-Methyl-2-pentene	99.3	325	35	468
Cyclohexene	83.9	305	35	444

In view of its low octane number, cyclohexene has unusually low cool-flame activity and high autoignition temperature.

Aromatics. The methyl derivatives of benzene resist low-temperature oxidation and do not undergo cool-flame reactions (*9, 14*). The autoignition reactions begin around 500° C. and increase steadily to ignition. Table I gives the autoignition temperatures, the temperature rises just before ignition, and the ignition delays for five methylbenzenes. Aromatics with higher autoignition temperatures tend to have lower temperatures rises and lower delays before ignition, but the trend is not pronounced. Other alkyl derivatives of benzene may give cool-flame reactions under unusual experimental conditions.

For aromatics that do not undergo cool-flame reactions in the engine, the knocking tendency is determined by autoignition reactions. Figure 7 shows a good linear

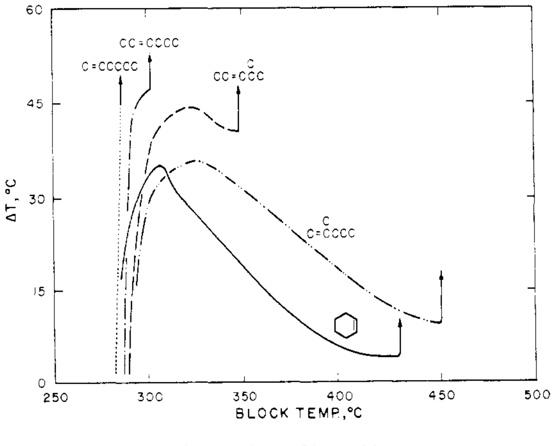

Figure 6. Thermal profiles of hexenes

Table I. Precombustion Properties of Methylbenzenes

Hydrocarbon	T_a, ° C.	DT, ° C.	Delay, Seconds
o-Xylene	539	20	7.6
Mesitylene	582	20	5.2
Toluene	625	22	5.2
m-Xylene	635	15	5.2
p-Xylene	638	10	5.0

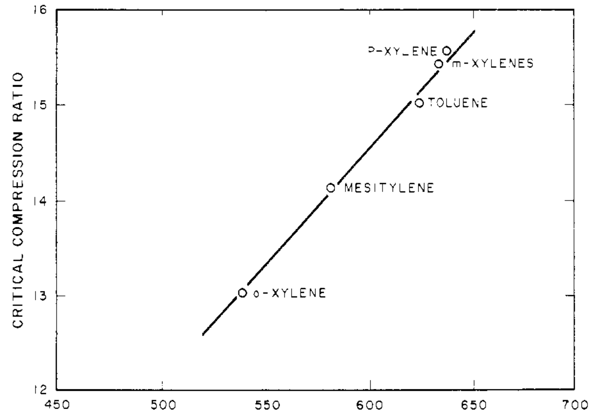

Figure 7. Ignition temperature and knocking tendency

correlation between the autoignition temperatures for methylbenzenes and knocking tendencies as measured by critical compression ratios (*6*). Other aromatics, however, show only qualitative correlations.

Blends of Aromatics in Iso-octane. The effect of various concentrations of aromatics upon the precombustion reactions of iso-octane is shown in Figure 8 by the thermal profiles for blends of ethylbenzene in iso-octane. Although the effect of ethylbenzene extends over the entire temperature range, cool-flame reactions are influenced most and are completely suppressed with about 50% of ethylbenzene in the mixture.

The magnitude of the inhibitory effect depends upon the chemical structure of the aromatic (*29*). The effects of varying concentrations of benzene, ethylbenzene, and mesitylene upon the cool-flame reactions of iso-octane are shown in Figure 9. Extrapolation of the curves to the abscissa gives the percentage concentrations for complete suppression of cool flames and, therefore, the relative effectiveness of the aromatics.

Extrapolated percentages for several aromatics are compared (Table II) with two other measures of reactivity.

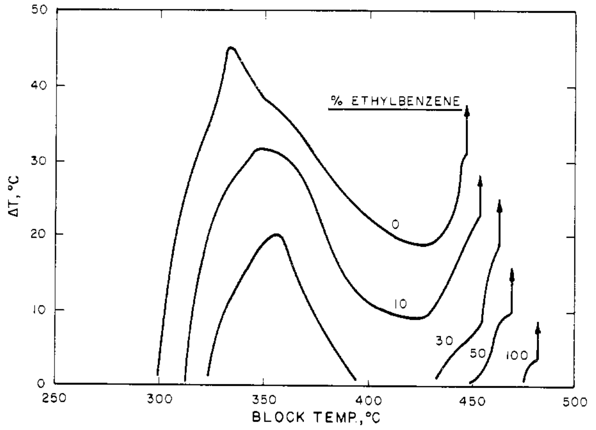

Figure 8. Thermal profiles of blends of ethylbenzene in iso-octane

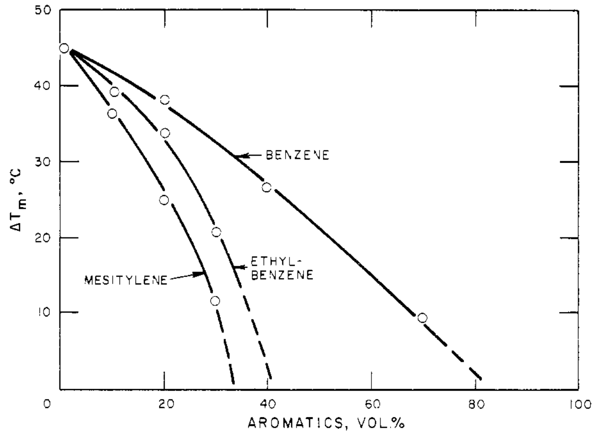

Figure 9. Effect of aromatics on cool flames

Both reactivity to *tert*-butoxy radicals (*28*) and blending octane values of 10% in iso-octane, rate the aromatics in essentially the same order. Reaction of *tert*-butoxy radicals with alkyl-substituted benzenes involves hydrogen abstraction from the side chains (*8, 30*), and inhibition of cool-flame reactions probably also occurs through hydrogen abstraction. The weak effect of benzene must be due mainly to dilution, as evidenced by the inability of benzene to increase temperatures at which exothermic reactions appear at maximum intensity for iso-octane.

Mixtures containing more aromatics than needed to supress cool-flame reactions undergo only autoignition. The autoignition temperatures seem to be unaffected by the inhibitory ability of the aromatics, but are depressed by iso-octane, which promotes autoignition of the aromatics. The extent of this effect determines the shapes of both ignition and octane-blending curves. Such curves are shown in Figure 10 for blends of benzene, ethylbenzene, and mesitylene in iso-octane. Despite the wide difference in conditions existing in the ignition apparatus and the internal-combustion engine, the similarity between the two types of curves suggests a common nature for the two phenomena.

INTERPLAY BETWEEN COOL FLAMES AND AUTOIGNITION

The similarity between the ignition and blending curves of the binary mixtures studied points again to the autoignition nature of knock. The effect of the cool-flame reactions in an engine seems to be mainly in raising the temperature of the fuel-air mixture above the temperature obtained by compression alone (*19*). Thus, hydrocarbons undergoing cool-flame reactions may reach their autoignition temperatures at lower compression ratios than those without cool-flame reactions. Diisobutylene has a lower autoignition temperature, but a higher octane number than iso-octane, because it does not undergo cool-flame reactions

Table II. Relative Reactivities of Aromatics

Hydrocarbon	Vol. %, To Suppress Cool-Flames	Reactivity to *tert*-BuO·	Blending Octane Values
Mesitylene	35	4.01	134
p-Xylene	35	3.05	135
Cumene	42	2.80	130
Ethylbenzene	44	2.30	130
Toluene	50	1.00	126
p-Chlorotoluene	55	0.71	120
Benzene	80	. . .	111

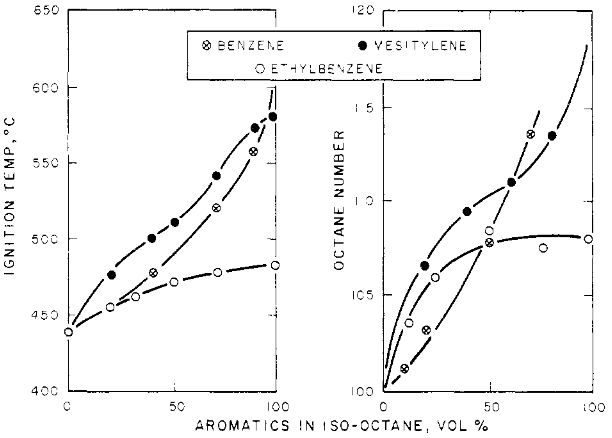

Figure 10. Relation between ignition temperature and octane number

in the engine (*26*). Furthermore, the peak in the octane-blending curve for iso-octane with diisobutylene blends (Figure 11) can now be explained by their mutual interactions. Diisobutylene raises the octane number of iso-octane by inhibiting its cool-flame reactions. Iso-octane, on the other hand, raises the octane number of diisobutylene by increasing its autoignition temperature. The two effects merge to produce the peak at about the concentrations of diisobutylene needed to completely suppress the cool-flame reactions.

CONCLUSION

Within each class of hydrocarbon, knocking tendencies correlate qualitatively with several properties of precombustion reactions. However, the octane numbers of all the hydrocarbons studied, regardless of class, correlate well only with the temperatures at which exothermic reactions appear and the temperatures at maximum intensity (Figure 12). Autoignition temperatures and cool-flame intensities do not correlate. Methylcyclohexane and 2-hexene with octane numbers of 91.3 and 92.7, respectively, ignite in the cool-flame region, whereas pentane and 2-methylpentane with octane numbers of only 62 and 73.4, respectively, do not generate enough heat for ignition. These two properties are greatly affected by the concentrations of both fuel and oxygen, so that the lack of agreement may result from limitations of the experimental method.

Notwithstanding the inherent restrictions of the ignition apparatus, the relations of hydrocarbons within each class are self-consistent and generally agree well with results by more sophisticated methods. The most serious difficulty is that of maintaining desired stoichiometric conditions because of the wide differences in boiling points and rates of evaporation of hydrocarbons. Therefore, comparison of precombustion properties of hydrocarbons across family groups can only be limited. To improve our understanding of knock, further studies under strictly controlled conditions in the laboratory must supplement investigations in engines.

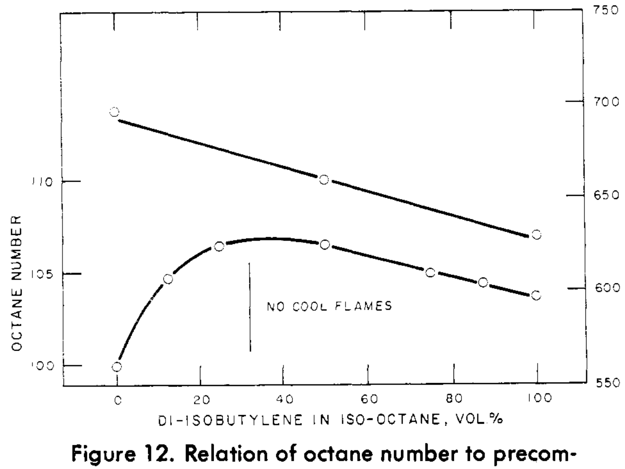

Figure 12. Relation of octane number to precombustion characterisitics

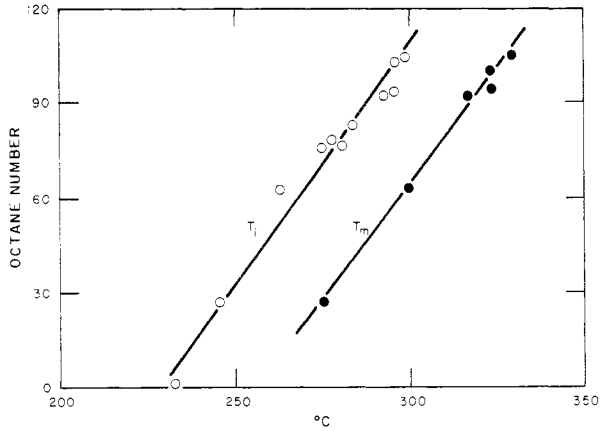

Figure 11. Interaction between di-isobutylene and iso-octane

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