Scientific Paper

Chemical Interpretation of Octane Number[†]

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[†] Dedicated to the memory of Prof. Dr. Davorin Dolar

Abstract

The empirical rules of Octane Number (ON) dependence on the structure of alkanes are amended. ON decreases with the number of CH_2 groups and increases with the number of CH_3 groups; the number of adjacent CH_2 groups has the highest but sigmoid influence; ON decreases with the separation between branches; it increases with the more central position of branches and with their bulkiness. Ethyl group causes apparently contradictory effects: If it increases the number of CH_2 groups, ON decreases; if not, ON increases. The use of structural features of alkanes, i.e. the size of the molecule, the number of branches, the position of branches, the separation between them, the type of branches, and the type of the branched structure enables a more thorough understanding of the relations between the structure of alkanes and their physicochemical properties. Comparison of kinetic and structural data of *n*-alkanes vs. branched alkanes indicates that in alkanes having a sufficient number (3 to 7) of adjacent CH_2 groups there exists the possibility of forming a limited number of *gem*-diperoxydiol groups, which may be responsible for knocking of low ON fuel - air mixtures.

Key words: *gem*-dihydroperoxide, hydroperoxide, octane number, polyperoxide, reaction mechanism, structural interpretation

1. Introduction

Octane number (ON) is a figure of merit representing the resistance of gasoline to premature detonation when exposed to heat and pressure in the combustion chamber of an internal-combustion engine.[1] It is measured against a prescribed binary mixture of isooctane (2,2,4-trimethylpentane, ON = 100) and *n*-heptane (ON = 0) under standard conditions.

The relation between the structure of hydrocarbons and their ON was studied using a number of topological indices. Well-known topological indices like e.g. the Wiener index did not prove sufficiently good, so several other indices or combinations of them were tested.[2-12] A physicochemical discussion about the meaning of ON on the molecular level, however, did not go beyond some empirical rules:[2,6,13-15]

i. ON increases with the number of tertiary and quaternary carbon atoms[2,6] resp. it increases with the number of methyl groups[13-15]

ii. It decreases with the total number of carbon atoms[2,6] resp. with the length of the chain[13-15]

iii. ON gets larger as the branching point is moving toward the center of the longest chain in the alkane molecule.

The "isoparaffin index", i.e. the ratio of CH_3/CH_2 groups content was also found to be an important measure of ON.[16] Whereas the most important is the content of CH_3 and CH_2 groups in an alkane, the importance of the quaternary carbon atoms and especially of the tertiary carbon atoms is much lower and ON is influenced first of all by conversion of secondary carbon atoms into primary ones.[17]

The knowledge of reaction mechanisms, their properties, their rate coefficients, etc, on the other hand, has grown enormously and it has been reviewed by Warnatz et al.[13]

In present work we are looking for additional structural explanations of ON values.

2. Data and Notations

Experimental data for Octane Number (ON) i.e. of Blending Octane Number (BON), Reasearch Octane Number (RON), and Motor Octane Number (MON) of alkanes were taken from Balaban and Motoc,[2] Hosoya,[6] Gutman et al.,[9] Warnatz et al.,[13] and Morley.[15] They are collected in Table 1. Estimated data[12] is marked with an asterisk: in Table 1 before its value (e.g. *92.1), whereas in Figures it is marked before the structural notation of the alkane in question (e.g. *2233M4). The data of vapor pressure of alkanes (logVP) were taken from Goll and Jurs.[18]

Table 1. Octane Number data

Alkane	BON[15]	RON[2,6,9]	MON[2,6,9]
Pr		112	
Bu	113	93.6	90.1
2M3	122	102	97.6
Pe	62	61.7	61.9
2M4	99	92.3	90.3
22M3	100	85.5	80.2
Hx	19	24.8	26
2M5	83	73.4	73.5
3M5	86	74.5	74.3
23M4	96	*92.1	94.4
22M4	89	91.8	93.4
Hp	0	0	0
2M6	41	42.4	46.4
3M6	56	52	55
3Et5	64	65	69.3
24M5	77	83.1	83.8
23M5	87	91.1	88.5
22M5	89	92.8	95.6
33M5	83	80.8	86.6
223M4	113	112.1	101.1
Oct	-19	-19	-19
2M7	13	21.7	23.8
3M7	30	26.8	35
4M7	31	26.7	39
3Et6	49	33.5	52.4
25M6	56	55.5	55.7
24M6	65	65.2	69.9
23M6	71	71.3	78.9
34M6	67	76.3	81.7
3Et2M5	76	87.3	88.1
22M6	67	72.5	77.4
33M6	73	75.5	83.4
3Et3M5	77	80.8	88.7
234M5	97	102.7	95.9
224M5	100	100	100
223M5	105	109.6	99.9
233M5	100	106.1	99.4
2233M4	*120	*137	*117
Non	-17		
26M7	*50		
225M6	91		
235M6	81		
3E22M5	108	112.1	
3E24M5	88	105.3	
2233M5	123	116.8	
2244M5	*118		
Dec	-41		
5M9	*2		
45M8	48		
27M8	20		
255M7	31		
335M7	77		
2345M6	*96		
2233M6	126		

* Estimated values[12]

The structures of alkanes are presented in shorthand, e.g. Hp is *n*-heptane, Oct is *n*-octane, 223M5 is 2,2,3-trimethylpentane, 3E2M5 is 3-ethyl-2-methylpentane, etc.

3. Relations Between ON Data

3.1. Relation with the vapor pressure

The values of MON and RON, Table 1, are in most cases close to one another, whereas some BON values deviate appreciably. This is most easily seen in Figure 1, where the difference BON - $^1/_2$(RON + MON) is plotted against logVP as a measure of their volatility. BON values of the most volatile alkanes (butanes, some pentanes, and hexanes), and as a surprise, also 3-ethylhexane, are higher than their MON and RON values, whereas BON values of the less volatile 2M7, 34M6, and 3E2M5 are lower.

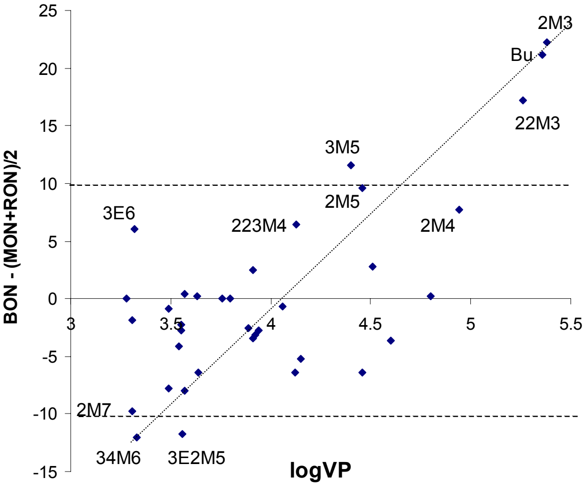

Figure 1. Relation between the deviation of BON from the mean of (MON and RON) vs. the vapor pressure of alkanes from *n*-butane to octanes inclusive.

If the BON values are affected by the volatility of alkanes, which results in unconsidered enrichment of the more volatile high ON component in the vapor phase, then one can reasonably expect, on the one hand, that to those highly volatile alkanes too high BON values are ascribed. On the other hand, however, one can reasonably expect also that some less volatile alkanes, including the higher *n*-alkanes, would not reach the expected concentration in the vapor phase during the test and consequently to them might be ascribed an inappropriate BON value due to their too low volatility compared to the standard alkane blend. If this reasoning is correct, then one has to await better experimental (injection) methods to obtain more reliable data. Until then, the probability of too high BON values of mentioned alkanes is to be taken into account.

3.2. Relation to the size of the unsubstituted part of the main chain of the alkane

The relation between available ON data of *n*-alkanes and their size, and consequently the number of adjacent methylene groups in their structure is presented in Figure 2.

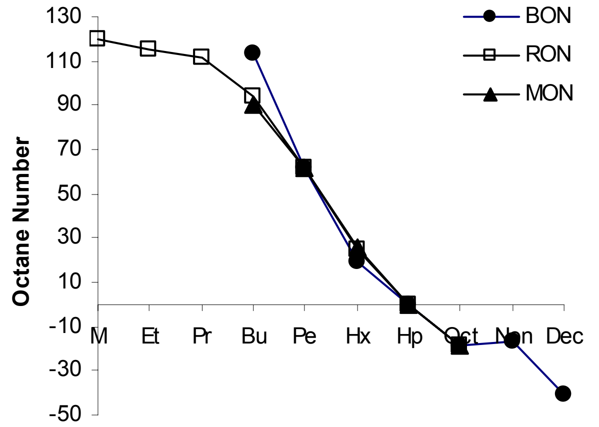

Figure 2. Decrease of ON with the size of *n*-alkanes.

The ON values taken together exhibit a decreasing sigmoid dependence on carbon number of *n*-alkanes. The reported[15] BON value of *n*-nonane (Non) seems to be an outlier. In the (estimated average rate) vs. BON plot of Morley,[15] *n*-nonane is an outlier as well, and the same can be observed there also for *n*-decane (Dec). Taking Morley's[15] k-values as a guide, the values $BON_{Non} = -27$ and $BON_{Dec} = -31$ would result, giving rise to an almost perfect lower part of the sigmoid curve.

This indicates that there may be also a problem with experimental ON values of *n*-nonane and *n*-decane as it was previously with *n*-octane,[6] where a too high ON value was previously ascribed to it.

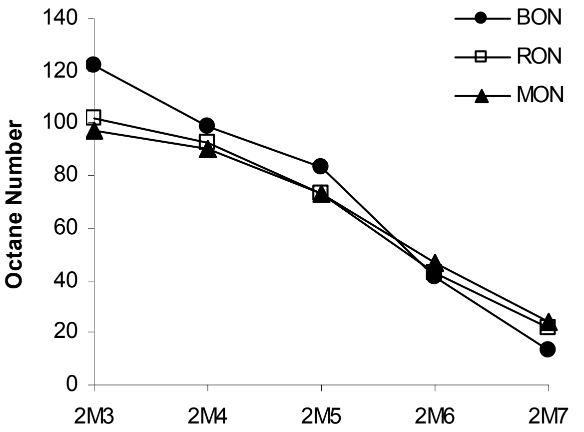

Figure 3. Decrease of ON with the size of 2-methylalkanes.

To a certain degree similar situation can be observed also among the 2-methyl- and 2,2-dimethylalkanes, Figure 3 and 4. In both cases, only the upper part of the supposedly sigmoid shape of dependence can be seen since the data of higher alkanes of this structure are lacking. On the other hand, on increasing the size of the main chain among 2-methylalkanes there can be observed a gradual decrease of ON, resembling the upper part of the sigmoid in Figure 1, whereas among 2,2-dimethylalkanes there can be observed first a slight increase, especially if we take into account the possibly too high BON value of 2,2-dimethylpropane.

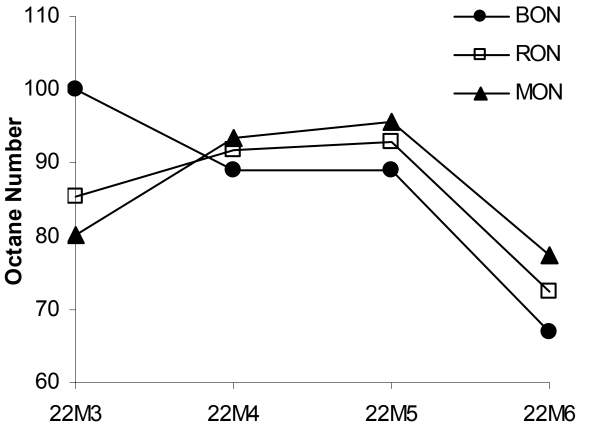

Figure 4. Decrease of ON with the size of 2,2-dimethylalkanes.

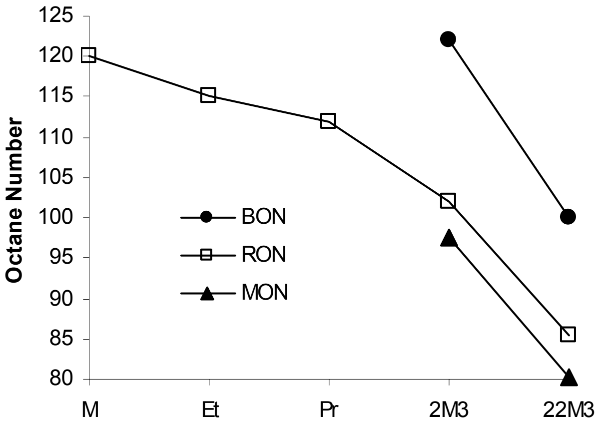

Figure 5. Decrease of ON with the increasing number of methyl branches on methane.

3.3. Relation with the number of branches

If the number of methyl branches on the methane carbon is increasing, Figure 5, the ON value of the resulting alkanes is lower and lower. Taking the butane backbone and increasing the number of methyl branching on it, Figure 6, the ON value first slightly decreases to reach its minimum (at BON; but if the

BON value of *n*-butane and 2-methylpropane is too high, this may actually not be the case) or it remains after adding the first two methyl groups nearly constant (RON and MON) and on addition of subsequent methyl groups it increases. Taking the pentane backbone, on the other hand, ON increases with increasing number of methyl groups, Figure 7-9, regardless of where they are positioned.

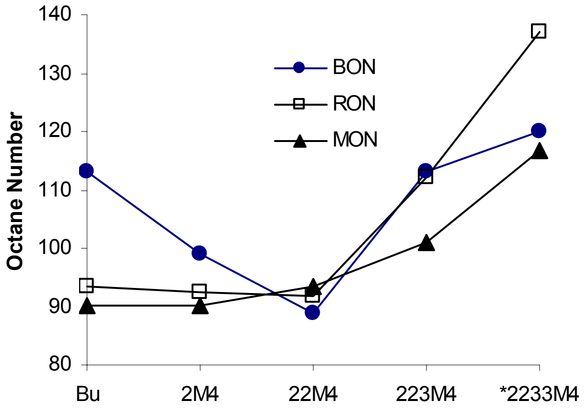

Figure 6. Variation of ON with the increasing number of methyl branches on the butane backbone.

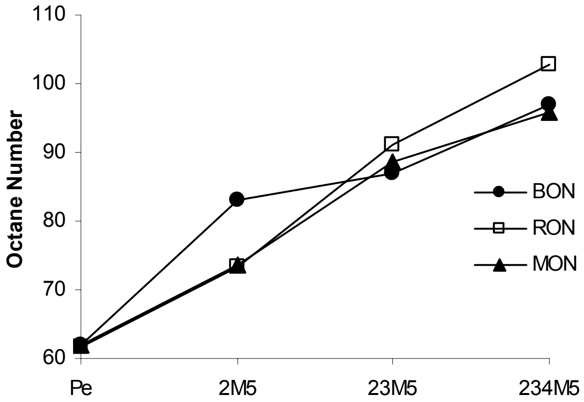

Figure 7. Variation of ON with the increasing number of methyl branches on the pentane backbone to give tertiary carbons.

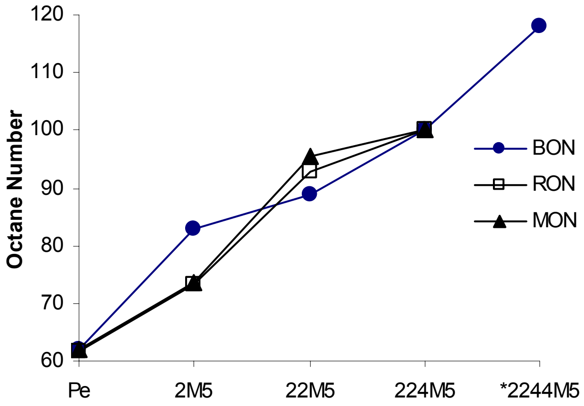

Figure 8. Variation of ON with the increasing number of methyl branches on the peripheral atoms on the pentane backbone.

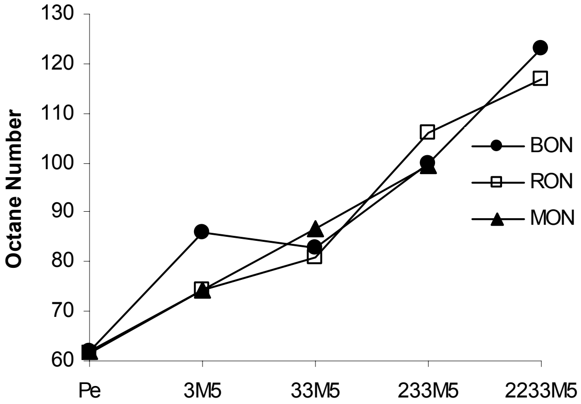

Figure 9. Variation of ON with the increasing number of methyl branches, first of all on the central atom on the pentane backbone.

3.4. Relation with the position of branches

Another question is, how the position of branches influences ON. It is a known fact[2,6,13-15] that ON gets larger as the branching point is moving toward the center of the longest chain in the alkane molecule. In methylheptanes, Figure 10, the more central position of the branch gives rise to higher ON, but the increase of ON is not linear. If we look at the series of alkanes having the central position of the methyl branch but differing in the size of the backbone, Figure 11, we can see that the larger is the backbone (i.e. the more adjacent methylene groups are contained in it) the lower are the ON values.

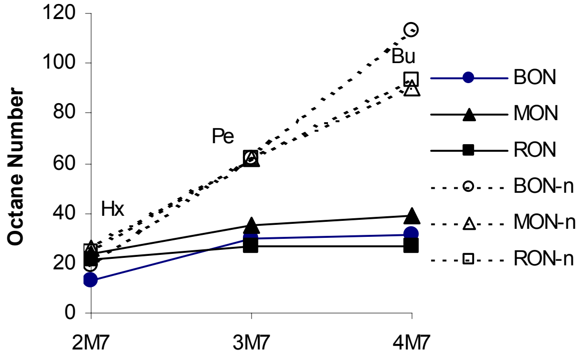

Figure 10. Increase of ON with the increasingly central position of methyl branches on the heptane backbone in comparison to *n*-alkanes having the same number of adjacent CH$_2$ groups.

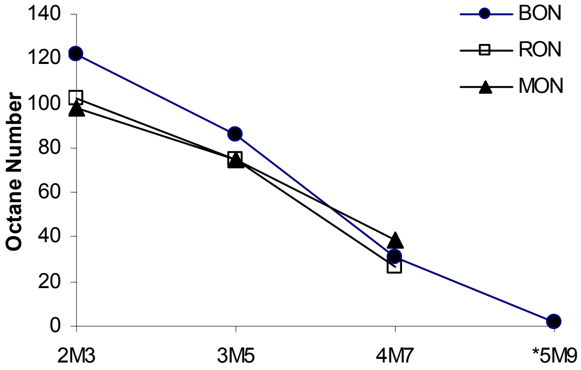

Figure 11. Decrease of ON with the size of the backbone in alkanes having the central position of methyl branches.

The same is supported by Figure 12, where dimethylhexanes with centrally positioned methyl groups have higher ON values than those with peripheral methyl groups.

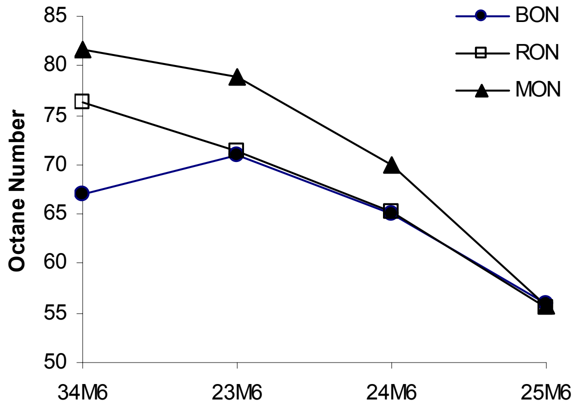

Figure 12. Decrease of ON with the increasingly peripheral position of methyl branches on the hexane backbone.

3.5. Relation with the separation between branches

In dimethylhexanes, Figure 12, it is also indicated that the change of the position of branches has a lower influence than their separation. Figure 13 supports the great influence of the separation (i.e. of the number of adjacent methylene groups) between branches. The pattern is to some extent similar to that in Figure 2, i.e. of *n*-alkanes of the same number of methylene groups.

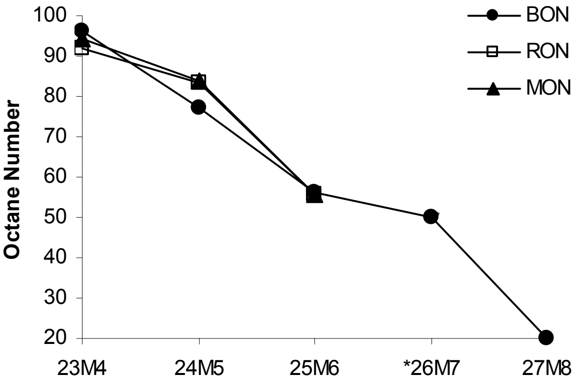

Figure 13. Decrease of ON with the increasing number of secondary carbons between the tertiary ones.

3.6. Relation with the bulkiness of the central branch

The influence of the bulkiness of the branch can be studied on centrally substituted pentanes, Figure 14. Here we can see that addition of a methyl group increases ON, whereas an ethyl group introducing an additional CH_2 group returns the value of ON close to the value of *n*-pentane. Transforming the secondary carbon of the ethyl group into a tertiary one of the *iso*-propyl group increases ON values again, whereas its transformation into the quaternary *tert*-butyl one gives rise to an additional increase.

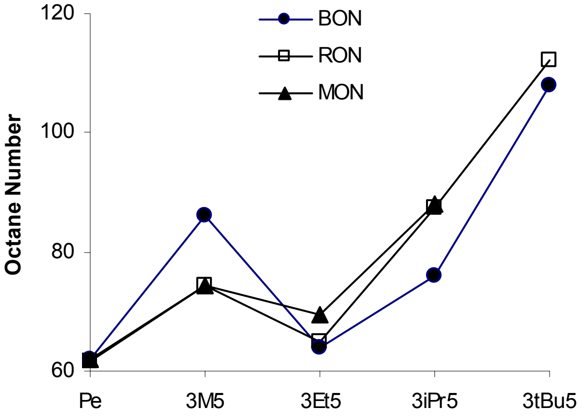

Figure 14. Variation of ON with the increasing bulkiness of branches on the central carbon of the pentane backbone.

Figure 15 presents an additional comparison of ON values of alkanes having methyl resp. ethyl groups on the pentane backbone. As a rule, the ON values of alkanes having an ethyl substituted pentane backbone instead of a methyl substituted one are lower. Thus, the decrease of the ON value by changing the branch type from methyl to ethyl keeping the same size of the alkane backbone seems to be a general rule.

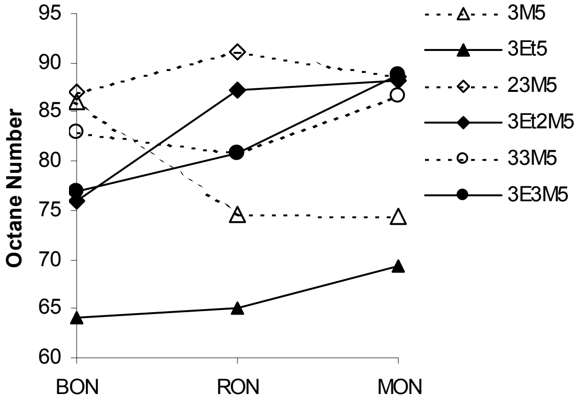

Figure 15. Comparison of ON values of alkanes having methyl or ethyl groups.

3.7. Relation with the number of adjacent tertiary carbons

Increasing the size of the alkane having only primary and tertiary carbons, Figure 16, seems to have in most cases little influence on ON.

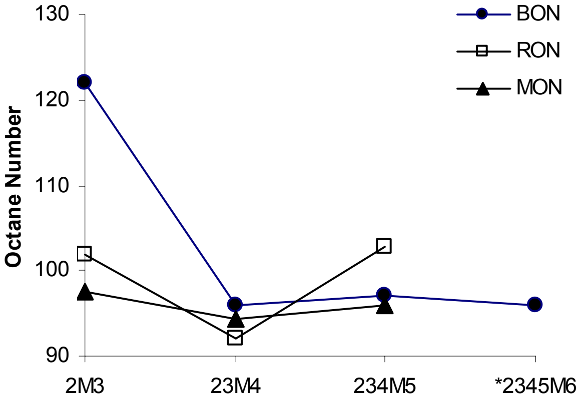

Figure 16. ON values of alkanes having only primary and tertiary carbons.

There are available too few data for alkanes having only primary and quaternary carbons. Some indication of the situation is presented in Figure 17.

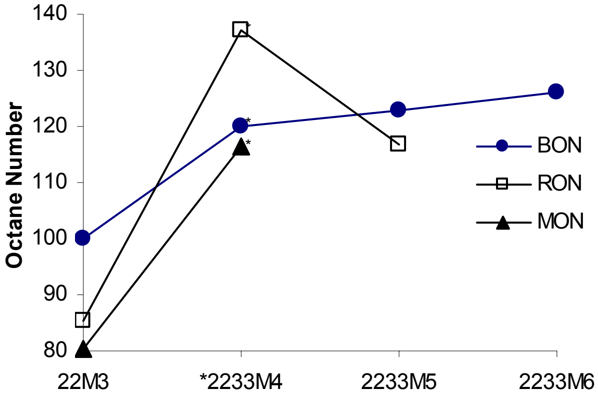

Figure 17. ON values of some alkanes having primary and quaternary carbons.

4. Discussion

From relations presented above follows as a rule of thumb, that the high ON values, i.e. ON ≥ approx. 100, are determined by the presence of primary and quaternary carbons. The intermediate ON values, i.e. around 90, are determined by the presence of tertiary carbons, Figure 16. The low values of ON, i.e. down to zero or below it are determined by the presence of several adjacent secondary carbons.

There remains an open question whether increasing the number of adjacent secondary carbons leads to an asymptotical approach to the linear decrease of ON values. The number of available ON data is still not sufficient to answer this question. In some cases, the data are lacking for low MW alkanes, whereas most experimental data are lacking for nonanes and decanes. The influence of alkane volatility on BON values, Figure 1, makes several data questionable and one has to await better experimental (injection) methods to obtain more reliable data.

If the values of BON of 2M3, Bu, 22M3, and 2M4 are really too high and those of 34M6 too low and if one allows for this discrepancy, then the trends in Figures 3, 4, 6, 12, 15, and 16 become consistent and can be interpreted. From Figure 3 follows that on increasing the number of secondary carbons in the main chain of the 2-methylalkanes the trend is similar to that among the *n*-alkanes of the same number of secondary carbons. Thus, the tertiary carbon in the 2-methyl group has little influence on the ON values, in agreement with correlation results.[17]

From Figure 4 follows, on the other hand, that the 2,2-dimethyl group containing a quaternary carbon exerts some ON-increasing influence to the nearest two secondary carbons, whereas the third one seems to follow the ON decreasing tendency as observed at *n*-alkanes and 2-methylalkanes. The explanation of the effect of the quaternary 2,2-dimethyl group is straightforward: the steric hindrance of it is felt two carbons far from its center and it decreases with distance as it could be expected. The steric hindrance of the tertiary 2-methyl group, on the other hand, is lower than that of the quaternary 2,2-dimethyl group. In addition, the 2-methyl group can be involved in the oxidative reactions and it can contribute to their propagation, whereas the quaternary C in the 2,2-dimethyl group cannot, till this group breaks down.

From Figure 6 would then follow that when the hydrogen atoms bound to the interior carbons in the butane backbone are substituted by methyl groups, then the first substitutions do not change the ON values appreciably, whereas the substitution of the last ones causes an appreciable increase. This seems to be between the situation in Figure 5, where the methyl substitution onto the methane carbon leads to decreasing ON values, and in Figure 7 - 9, where the substitution of the pentane backbone leads to a steady increase of ON values regardless of where the additional methyl group is placed.

The ON decrease observed in Figure 5 can be explained by the increasing effect of hyperconjugation as well as by the increasing number of methyl groups in the β position. The comparison of Figure 5 with Figure 17, where the methyl groups on adjacent quaternary carbons are in γ positions indicates the importance of the distance between the methyl groups when no secondary or tertiary groups are placed between them. The patterns observed in Figures 6-9 call for additional effects in order to be explained. One of them is the number of hydrogen atoms that are easily abstracted in an intramolecular reaction (on CH_2 or CH groups, especially in the β position). The other one is the increasing steric hindrance.

That the sterical hindrance is an important feature influencing ON follows not only from Figure 4 and 16 but also from Figure 13, where the increasing bulkiness of the substituent on the same (pentane) backbone increases ON. An exception is the ethyl group, which introduces not only additional steric hindrance, but also an additional secondary carbon. It seems as if the additional secondary carbon had the opposite effect but of the same magnitude as the bulkiness of the ethyl group. Cf. also Figure 17.

It was known far ago[14] that the more central position of the methyl substituent within the alkane backbone gives rise to a higher ON value. This is illustrated also in Figures 10 and 12. But if the backbone of the alkane gets longer, the ON values decrease, Figure 11. If, on the other hand, at the same length of the alkane backbone the central substituent gets bulkier, Figure 14, then the ON value increases. An exception is the ethyl group, which introduces an additional CH_2 group, which lowers the ON value.

Figure 12 indicates also that the position of branches is less important than their separation. The influence of the separation of branches is demonstrated also in Figure 13.

The approach used above has also a side effect. Namely, if we include into above-mentioned relations also some estimated[12] ON data, then we can see whether an estimated value is probable or not. For example, in Figure 6 and 17 seems the estimated BON value of 2233M4 quite probable. The same is the impression in Figure 8 for BON of 2244M5, in Figure 11 for BON of 5M9, as well as in Figure 16 for BON of 2345M6. In Figure 13, however, the estimated BON value of 26M7 seems to be too high.

On the other hand, the above explanations confirm the usefulness of the approach using structural features[20,21] of alkanes for structural interpretation of their physicochemical properties.[22]

Although this type of relations is complex, even its simple linear approximation[23-32] gives an approximate insight into the importance and direction of contribution of a particular structural feature to the physicochemical property in question.[32]

Table 2. Linear approximation of the contribution of structural features[32] to the ON values.

	Derivation	BON	RON	MON
b	33M6 - 3M7	43	48.7	48.4
c	34M6 - 23M6	-4	5	2.8
s	24M6 - 23M6	-6	-6.1	-9
e	3Et2M5 - 23M6	5	16	9.2

b - contribution of the number of branches
c- contribution of the more central position
s - contribution of separation between branches
e - contribution of change of a methyl group into an ethyl one

For the ON data, the influence of the size of the molecule is illustrated e.g. in Figure 2 and 13. The simple linear approximation of the influence of other structural features is presented in Table 2.

In Table 2 can be seen that at the same size of the alkane molecule, the number of methyl branches has the highest contribution to the increase of ON. Regarding the position of branches, we should have in mind the situation in Figure 1, where the BON value of 34M6 is indicated to be too low compared to RON and MON values. If we look at RON and MON, we see that the more central position of branch gives rise to slightly higher ON values, in accordance to Figure 10 and previous statements.[2,6,13-15] Larger separation between branches gives rise to a decrease of ON, and this to a higher degree than the increase due to the more central position. This is in accordance with Figure 13. The increase of ON in Table 2 on conversion of a methyl branch into the ethyl one at the first look contradicts the observation in Figure 14. But here we have two different situations. Namely, in Figure 14 the main chain of the alkane remains the same and the number of CH_2 groups increases. In the situation presented in Table 2, however, when the methyl group is replaced by an ethyl one, the main chain is simultaneously shortened by one CH_2 group, so that the total number of them remains the same, but the molecule becomes more branched and as the consequence ON increases.

There remains without the answer a crucial question, namely why on increasing the number of CH_2 groups ON appreciably decreases, Figure 2 and 13, whereas in their absence on increasing the number of (tertiary) CH groups, Figure 16, it remains nearly constant and on increasing the number of quaternary carbons, Figure 17, it increases.

One answer is straightforward: Quaternary carbons are not involved in oxidative reactions till the quaternary structure breaks down. Until then, the reactions take place only on their neighbor atoms. On the other hand, these neighbor atoms of the quaternary carbons, which are in most considered cases the methyl groups, give rise to an appreciable sterical hindrance. Thus, there remains the question, why is the contribution of CH_3, CH_2, resp. CH groups so different.

The answer to the last question is to be sought for in the reactions possible in these functional groups. Several reactions are well established.[13] In the case of *n*-heptane, for example, there are known 2400 reactions, 620 products and a number of kinetic parameters of these reactions.[19]

The most important steps in the reaction mechanism based on modeling by previous authors were presented by Morley.[15] In *n*-pentane, for example, is the most important the sequence of reactions presented in Figure 18.

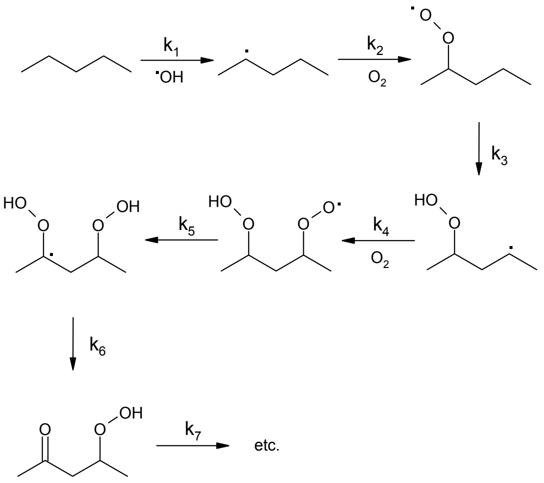

Figure 18. Some of the reaction steps in *n*-pentane.[15]

At a typical T = 625 K,[13] the rate constants calculated from equations presented by Chevalier et al.[19] are as follows in Table 3.

Table 3. Kinetic constants (s^{-1}) of the most important reactions of alkanes, calculated for T = 625 K from equations in Ref.[19]

Reaction	CH_3	CH_2	CH
$RH + O_2 \rightarrow R^{\cdot}$	3.00×10^{-5}	1.60×10^{-4}	1.60×10^{-4}
$RH + {}^{\cdot}OOH \rightarrow R^{\cdot}$	3.04×10^{5}	1.89×10^{6}	9.14×10^{6}
$RH + {}^{\cdot}OH \rightarrow R^{\cdot}$ (k_1)	2.87×10^{11}	1.15×10^{12}	2.80×10^{12}
$HpOO^{\cdot} \rightarrow {}^{\cdot}HpOOH$			
$C(2)OO^{\cdot} \rightarrow \alpha C(3)^{\cdot}$	4.14×10^{3}	4.64×10^{4}	2.32×10^{5}
$C(2)OO^{\cdot} \rightarrow \beta C(4)^{\cdot}$ (k_3)	1.16×10^{6}	1.31×10^{7}	
$C(2)OO^{\cdot} \rightarrow \gamma C(5)^{\cdot}$	4.14×10^{3}	4.64×10^{4}	3.04×10^{5}
${}^{\cdot}OOHpOOH \rightarrow HOO^{\cdot}HpOOH$			
$C(2)OO^{\cdot} \rightarrow \alpha C(3)^{\cdot}$	6.71×10^{3}	1.13×10^{5}	1.89×10^{6}
$C(2)OO^{\cdot} \rightarrow \beta C(4)^{\cdot}$ (k_5)	7.78×10^{5}	1.31×10^{7}	
$C(2)OO^{\cdot} \rightarrow \gamma C(5)^{\cdot}$	5.64×10^{5}	6.32×10^{6}	7.09×10^{7}
$C(2)OO^{\cdot} \rightarrow \delta C(6)^{\cdot}$	4.00×10^{2}	6.71×10^{3}	

For $R^{\cdot} + O_2$, T < 900 K, $k = 2\times10^{12}\ cm^3mol^{-1}s^{-1}$.[33] ($k_2$), ($k_4$)

The comparison of kinetic constants at 625 K shows that the most effective starting reaction is RH + ˙OH, which is very fast, k ~ $10^{12}\ s^{-1}$. It is followed by the reaction RH + ˙OOH, having k ~ $10^{6}\ s^{-1}$. The reactivity of functional groups in alkanes is in general CH (tertiary) > CH_2 (secondary) > CH_3 (primary). The higher the alkane, the less important is the intermolecular H abstraction.[19] Intramolecular H abstraction is the fastest from the second (i.e. the β) carbon counted from the OO˙ group-bearing one, but also the rate of abstraction from the adjacent (i.e. the α) one as well as from the third (i.e. the γ) one is appreciable.

Most authors follow Pollard,[34] who assumed that the release of the first ˙OH from ˙OOR"OOH leads to the formation of a carbonyl group, via internal rearrangement of the molecule with k = 2.37×10^{6} s^{-1} at 625 K (k_6), whereas the second release has k = $7.54\times10^{-1}\ s^{-1}$ at 625 K (k_7). From data in Table 3 follows that the kinetic constant of internal H abstraction from secondary or tertiary β-carbons is higher than the kinetic constant of scission of the already formed hydroperoxide groups by a factor of 2 to 30. This means that there exists appreciable chance that the third and possibly also some subsequent internal H abstraction takes place, before the scission of the already formed hydroperoxide groups followed by subsequent rearrangement of the molecule comes to effect.

The abstraction from the methyl groups, on the other hand, is in any case slower than the scission of already formed hydroperoxide groups, by a factor of 3 up to several orders of magnitude. This means that in the first approximation we can neglect not only the contribution of the quaternary carbons but also of the methyl groups. Doing so, we can try to understand the reasons for the pattern in Figure 7 and 16. Let us look for the possible reactions in *n*-pentane and in 2,3,4-trimethylpentane.

n-Pentane and 2,3,4-trimethylpentane differ i.a. in two characteristics: The number of slow reacting[15] CH_3 groups that can be released subsequently, as well as in the number of H atoms that can be abstracted and replaced by a OO˙ group.

In 2,3,4-trimethylpentane the fast reactions end after two or at most three internal H abstractions and then follows the decay assumed by Pollard.[34]

In *n*-pentane, on the other hand, regarding the kinetic data presented above, after the second intramolecular H abstraction is quite probable also a third one, followed either by scission of the

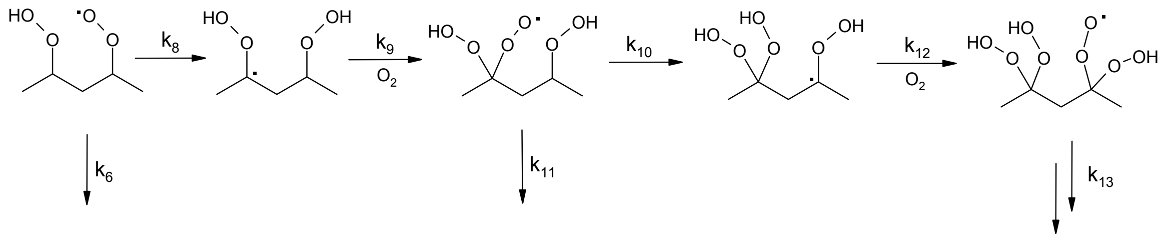

Figure 19. Hypothetical reaction sequence, which based on kinetic data of Table 3 seems possible to occur between step 4 and step 6 in Figure 18.

product in accordance to the assumption of Pollard,[34] or by O_2 addition giving rise to 2,2,4-pentane-trihydroperoxide, or in the next step even to 2,2,4,4-pentane-tetrahydroperoxide, both of which are analogues of peroxyketals, Figure 19.

If it is true[19] that $k_8 \sim k_3 \sim k_5$ and consequently also $\sim k_{10}$, as well as $k_8 > k_6$, then we have a plausible explanation for appreciable knocking tendency of higher *n*-alkanes. The tris- and tetra-hydroperoxides can be reasonably expected to be more amenable to cause the detonations (releasing three to four $^{\cdot}$OH radicals, which can induce reactions on other *n*-alkane molecules) characteristic for *n*-pentane (and *n*-heptane),[35] than the 2,4-pentane dihydroperoxide with its approx. $k_5 = 2.37\times10^6$ s^{-1} and $k_6 = 7.54\times10^{-1}$ s^{-1} at 625 K.

There exists an analogy to the explosive decomposition of triacetone-triperoxide. The explosion of triacetone-triperoxide is not a thermochemically highly favored event. It rather involves entropy burst, which is the result of formation of four molecules from every triacetone-triperoxide molecule in the solid state.[36] If we compare from this point of view the 2,3,4-trimethylpentane-2,4-dihydroperoxide with 2,2,4-pentane-trihydroperoxide and 2,2,4,4-pentane-tetrahydroperoxide, then there can be formed 3 to 4, 4 to 6, and 5 to 7 new molecules from one molecule of the peroxy compound, respectively. Of these new molecules, there can be expected 2, 3, and 4 fast initiating OH radicals, respectively. From 2,2,4,4,6,6-heptane-hexahydroperoxide, 6 OH radicals and altogether 7 to 9 molecules could be formed. The number of molecules taking place in the reaction of a *n*-pentane molecule, Figure 18 and 19, resp. being formed after the decomposition of the peroxidic product is $6 \rightarrow 2 \rightarrow 5$ to 7, whereas on reaction of a *n*-heptane molecule it is $8 \rightarrow 2 \rightarrow 8$ to 10, comparable to $1 \rightarrow 4$ in triacetone-triperoxide. These data indicate the possibility of a local implosion as a consequence of fast binding of several oxygen molecules to a *n*-alkane molecule, followed by a local explosion after the fast decomposition of the peroxidic product induced by the implosion shock.

Since the number of intramolecular H-abstraction–O_2-addition steps is limited by the rates of other reactions taking place simultaneously, this fact may be an additional explanation in favor of the sigmoid shape in Figure 2 and not of the linear decrease of ON with the number of adjacent CH_2 groups.

In this way, considering the kinetic data in Table 3, we have a chemical explanation of Octane Numbers of alkanes. Quaternary carbons are not involved in oxidative reactions till the quaternary structure breaks down. Until then, their neighbor atoms exert sterical hindrance slowing down several reactions. The reactions take place only on their neighbor atoms, and the quaternary carbons get involved in the reactions at later stages. The hydrogen abstraction from primary carbons (CH_3 groups) is relatively slow and it determines the possible upper limit of ON values of alkanes, which is higher when the methyl groups are more than two bonds apart. The hydrogen abstraction from a tertiary carbon (CH group) is the fastest but only one hydrogen can be abstracted from it and consequently only one hydroperoxide group can be formed on it, which has as the consequence an appreciable ON value of around 90 when only tertiary and primary carbons are present. From secondary carbons, however, respecting the kinetic data, up to two hydrogen atoms can be abstracted before the formed peroxidic products disintegrate, especially if secondary carbons are in sterically non-hindered β-positions, where the intramolecular abstractions are the fastest. Fast binding of several oxygen molecules to form a peroxidic product causes a local implosion. Then follows the decomposition of the peroxidic product into a number of molecules, of which there are released up to two fast initiating OH radicals per secondary carbon. This sequence of events seems to be the reason for low ON values and high knocking tendency of alkanes having several adjacent CH_2 groups in their structure.

5. Conclusions

The empirical rules of Octane Number dependence on the structure of alkanes can be amended to become as follows:

- ON decreases with the number of CH_2 groups and increases with the number of CH_3 groups; the number of adjacent CH_2 groups has the highest but sigmoid influence;
- ON decreases with the separation between branches;
- ON increases with the more central position of branches;
- ON increases with the bulkiness of the branched structure;
- Ethyl group as a branch can express apparently contradictory effects: If it increases the number of CH_2 groups, ON decreases; if not, ON increases.

The use of structural features of alkanes, i.e. the size of the molecule, the number of branches, the position of branches, the separation between them, the type of branches, and the type of the branched structure enables a more thorough understanding of the relations between the structure of alkanes and their physicochemical properties.

Comparison of kinetic and structural data of *n*-alkanes vs. branched alkanes indicates that in alkanes having a sufficient number (3 to 7) of adjacent CH_2 groups there exists the possibility of forming a limited number of *gem*-dihydroperoxide groups, which may be responsible for premature detonations of low-ON fuel - air mixtures.

6. References and Notes

1. The Columbia Encyclopedia, Sixth Edition, 2001.
2. A. T. Balaban, I. Motoc, *MATCH (Commun. Math. Chem.)* **1979**, *5*, 197–218.
3. A. T. Balaban, *Theor. Chim. Acta* **1979**, *5*, 239–261.
4. A. T. Balaban, *Pure Appl. Chem*. **1983**, *55*, 199–206.
5. A. T. Balaban, L. B. Kier, N. Josh, *MATCH (Commun. Math. Chem.)* **1992**, *28*, 13–27.
6. H. Hosoya, *Croat. Chem. Acta* **2002**, *75*, 433–445.
7. M. Randić, *J. Math. Chem*. **1991**, *7*, 155–168.
8. M. Randić, *Acta Chim. Slov*. **1997**, *44*, 57–77.
9. I. Gutman, W. Linert, I. Lukovits, Z. Tomović, *J. Chem. Inf. Comput. Sci*. **2000**, *40,* 113–143.
10. S. Nikolić, D. Plavšić, N. Trinajstić, *MATCH (Commun. Math. Computer Chem.)* **2001**, *44*, 361–386.
11. B. Ren, *J. Chem. Inf. Comput. Sci*. **1999**, *39,* 139–143.
12. A. Perdih, F. Perdih, *Acta Chem. Slov.* **2006**, *53*, 180–190.
13. J. Warnatz, Combustion: physical and chemical fundamentals, modeling and simulation, experiments, pollutants formation, J. Warnatz, U. Maas, R. W. Dibble, 2nd Ed., Springer, Berlin etc 1999.
14. W. Lovell, *Ind. Eng. Chem*. **1948**, *40*, 2388–2438.
15. C. Morley, *Combust. Sci. Technol*. **1987**, *55*, 115–123.
16. M. E. Myers, J. Stollsteimer, A. M. Wims, *Anal. Chem*. **1975**, *47*, 2301–2304.
17. A. Perdih, M. Perdih, *Acta Chim. Slov*. **2000**, *47*, 57–77.
18. E. S. Goll, P. C. Jurs, *J. Chem. Inf. Comput. Sci*. **1999**, *39*, 1081–1089.
19. C. Chevalier, J. Warnatz, H. Melenk, *Ber. Bunsenges. Phys. Chem*. **1990**, *94*, 1362–1367.
20. D. Bonchev, N. Trinajstić, *J. Chem. Phys*. **1977**, *67*, 4517–4533.
21. E. C. Kirby, *J. Chem. Inf. Comput. Sci*. **1994**, *34*, 1030–1035.
22. A. Perdih, B. Perdih, *Indian J. Chem*. **2003**, *42A*, 1219–1226.
23. A. Perdih, B. Perdih, *Acta Chim. Slov*. **2002**, *49*, 67–110
24. A. Perdih, B. Perdih, *Acta Chim. Slov*. **2002**, *49*, 291–308
25. A. Perdih, B. Perdih, *Acta Chim. Slov*. **2002**, *49*, 309–330
26. A. Perdih, B. Perdih, *Acta Chim. Slov*. **2002**, *49*, 467–482
27. A. Perdih, B. Perdih, *Acta Chim. Slov*. **2002**, *49*, 497–514.
28. A. Perdih, B. Perdih, *Acta Chim. Slov*. **2003**, *50*, 83–94.
29. A. Perdih, B. Perdih, *Acta Chim. Slov*. **2003**, *50*, 95–114.
30. A. Perdih, B. Perdih, *Acta Chim. Slov.* **2003**, *50*, 161 – 184.
31. A. Perdih, B. Perdih, *Acta Chim. Slov*. **2003**, *50*, 513–538.
32. A. Perdih, B. Perdih, *Indian J. Chem*. **2003**, *42A*, 1246–1257.
33. S. W. Benson, *Progr. Energy Combust. Sci*. **1981**, *7*, 125–134.
34. R. T. Pollard, Comprehensive Chemical Kinetics, Vol. 17, Gas Phase Combustion (C. H. Bamford and F. H. Tipper Eds.), Elsevier, New York 1977.
35. M. Pechard, Technical Memorandums, National Advisory Committee for Aeronautics, No. 916, Washington 1939; http://naca.larc.nasa.gov/reports/1939/naca-tm-916/.
36. F. Dubnikova, R. Kosloff, J. Almog, Y. Zeiri, R. Boese, H. Itzhaky, A. Alt, E. Keinan, *J. Am. Chem. Soc*. **2005**, *127*, 1146–1159.

Povzetek

Izboljšana so empirična pravila o odvisnosti oktanskega števila alkanov od njihove strukture. Le-to pada s številom CH_2 skupin in narašča s številom CH_3 skupin; najbolj vplivajo sosednje CH_2 skupine. Pada z razdaljo med vejami, narašča pa z bolj sredinsko lego vej in njihovo razvejanostjo. Etilne skupine dajo navidezno nasprotujoče učinke: če povečajo število CH_2 skupin, oktansko število pade, če ne, pa naraste. Uporaba strukturnih značilnosti alkanov, to so velikost molekule, število vej, njihova lega, razdalja med njimi, njihova vrsta in vrsta razvejanosti, omogoča temeljitejše razumevanje odnosov med njihovo strukturo in lastnostmi. Primerjava kinetičnih in strukturnih podatkov za *n*-alkane in razvejane alkane kaže, da pri alkanih, ki imajo dovolj (3 do 7) sosednjih CH_2 skupin, obstoja možnost tvorbe omejenega števila *gem*-diperoksidiolnih skupin, ki bi lahko bile vzrok klenkanja v motorju.