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# PROBLEMS AND PROSPECTS OF FIRE PREVENTION AND EXTINGUISHING

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Research article

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## IMPACT OF CYCLIC HYDROCARBONS' STRUCTURE ON AUTO-IGNITION TEMPERATURE

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*Abstract.* Using experimental data available in the literature the impact of the molecular structures of cycloalkanes and aromatic hydrocarbons on the auto-ignition temperature is analyzed. Based on contemporary studies of auto-ignition kinetic processes of cyclic nonaromatic and aromatic hydrocarbons, the connection between chemical structure, bond strength in the molecule and features of radical mechanisms of oxidation processes with the auto-ignition temperature is shown. It is noted that unsubstituted cycles usually have the highest auto-ignition temperature. The increase in the structure of substituents the number of methyl groups and double bonds capable to conjugate with benzene ring contributes to an index increase. Alkyl side chains located in the ortho-position, as well as the elongation of the chain of alkyl radicals attached to the ring, reduce the auto-ignition temperature. Polycyclic aromatic structures have a lower auto-ignition temperature than structurally similar benzene derivatives.

*Keywords:* cycloalkanes, aromatic hydrocarbons, auto-ignition temperature, fire hazard

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### Introduction

Auto-ignition temperature ( $t_{AIT}$ ) is the lowest temperature necessary for substance's ignition without an external source. Based on thermal ignition theory and on classical reaction rate theory,  $t_{AIT}$  can be considered as the temperature, to which the combustible mixture must be heated so that the heat release rate resulted from exothermic oxidation reactions exceeds the rate of heat loss to the environment. Being a general indicator of fire hazard, according to GOST 12.1.044–89, the auto-ignition temperature is also included in international Material Safety Data Sheets (MSDS) [1, 2].

Since the experimental determination of this indicator is not always possible and is a complex and expensive process, numerous attempts have been made to derive mathematical laws that make it possible to calculate  $t_{AIT}$  of compounds. Russian scientific literature describes several calculation methods based on the structure and content of compounds. For hydrocarbons, acceptable accuracy was achieved only for linear, unbranched gaseous and liquid alkanes. In other cases, the declared error varies between 40–70 °C, which is substantially high and may lead to spontaneous combustion during transportation or operation of substances, especially since in real conditions, depending on external factors, namely volume and material of the vessel,  $t_{AIT}$ , may have even lower value [2–4].

The lack of scientific data regarding  $t_{AIT}$  significantly influences utilization of cyclic hydrocarbons. Cycloalkanes and arenes compose oil, motor and jet fuels and are used as an additive to improve their quality. By catalytic reforming, benzene derivatives are obtained from cycloalkanes, without which pharmaceuticals, production of explosives, high-molecular compounds and plastics is impossible.

Aromatic hydrocarbons, one of the most important classes of hydrocarbons used in motor fuels, play a key role in combustion processes in engines, determining the octane number and combustion efficiency. Arenes found in gasoline are generally monoaromatic, and condensed rings are used in jet and diesel fuels. Substituted alkylbenzenes with short side chains are used as anti-knock component to increase the octane number of gasoline; alkylbenzenes with long side chains improve the auto-ignition of diesel fuel.

Attempts to derive mathematical correlations for calculating the auto-ignition temperature of cyclic hydrocarbons have mainly been carried out in recent decades by foreign scientists. By using computer programs, entering a large amount of statistical data and breaking the molecule into structural descriptors, scientists from Taiwan, Iran, and the USA propose acceptable (in terms of accuracy) indicator values [5–9]. However the analysis of these works carried out by I.I. Baskin and his colleagues demonstrated that, despite stated accuracy of calculations, aforementioned values often do not correspond to experimental data [10]. Russian scientists believe that it is not possible to derive satisfactory mathematical correlations for aromatic compounds [11].

Another downside of these published studies is that the authors do not explain the dependences obtained when changing the structure of a substance from a chemical point of view, when they use statistical data and computer programs to derive calculation formulas.

The purposes of this research are the following:

- collection and processing of reference data on the auto-ignition temperature of cyclic hydrocarbons;
- analysis of the processes occurring during the auto-ignition of cycloalkanes and arenes, and the search for interdependencies between the structure and auto-ignition temperature on the basis of existing scientific data.

### Research methods

Kinetic features of the process and data on auto-ignition temperatures for cyclic hydrocarbons of different structures are collected, processed and presented in the form of tables and graphs, which make it possible to predict the  $t_{AIT}$  range for cycloalkanes and arenes of similar structure.

### Study results

The process of auto-ignition is radical; its speed, and thus the time to reach the temperature at which auto-ignition occurs, largely depends on the strength of the bonds in the molecule and the rate of radicals' accumulation in the system. The auto-ignition temperature of cycloalkanes is higher than that of alkanes due to the formation of a stronger cyclic structure. With an increase in the number of carbon atoms in the cycle,  $t_{AIT}$  decreases, and, just like for alkanes, it increases during the transition from liquid to solid state (fig. ). Thus, for cyclooctane, which has a melting point of 14,8 °C,  $t_{AIT}$  is 275 °C, and for cyclododecane, which melts at 62 °C,  $t_{AIT}$  is 350 °C [12].

It must be noted, that the  $t_{AIT}$  of cyclic alkanes is not affected by the tension in the cycle. As a fact, it decreases in the homologous series from cyclopropane to cyclohexane, in which the cycle tension energy is zero, then it increases again to C<sub>10</sub>, and then decreases. This dependence is represented in the combustion heat of cycloalkanes per methylene group, which reaches a minimum value in cyclohexane and then begins to increase, reaching a maximum value in cyclononane [13].

As Chinese researches have shown, the most resistant substances are unsubstituted rings or rings containing methyl groups as radicals [14]. As the length of the substituent increases or its isomerization, the strength of the molecule changes, as with alkanes, depending on the structure of the radical, which is confirmed by experimental data (table 1) [3, 12].

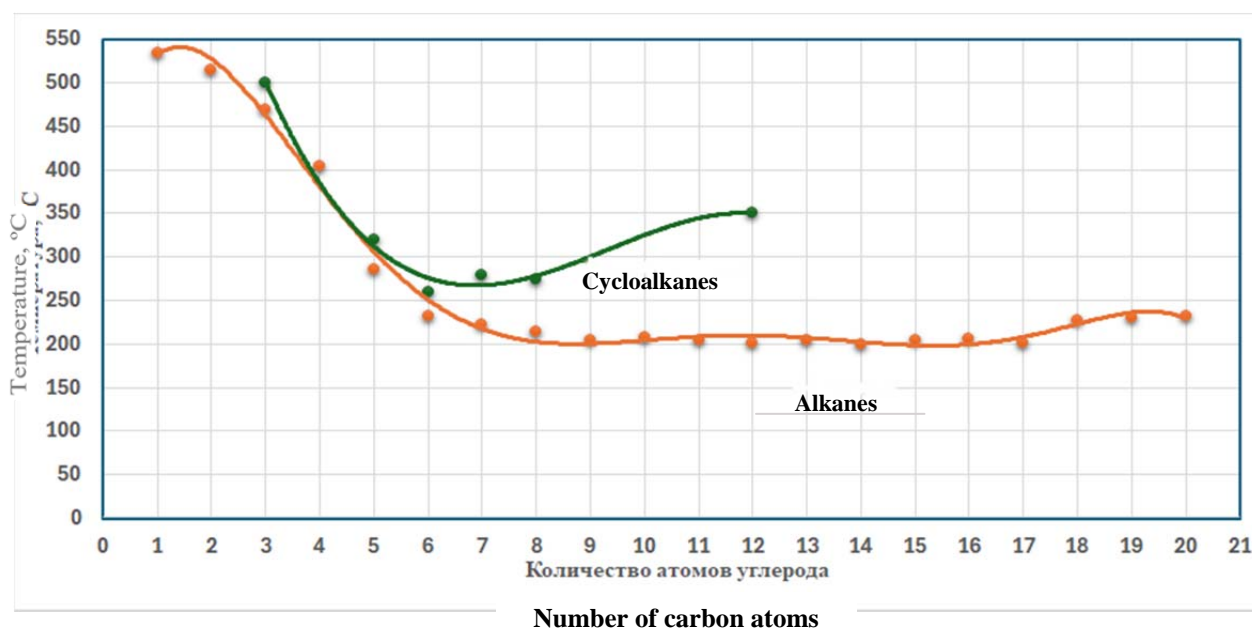


Fig. Dependence of the auto-ignition temperatures of n-alkanes and unsubstituted cycloalkanes on the number of carbon atoms in the chain

Table 1

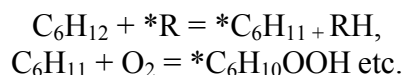
#### Auto-ignition temperature of cycloalkanes of various structures [3]

Unsubstituted cycloalkanes	Auto-ignition temperature, °C	Cyclohexane derivatives	Auto-ignition temperature, °C
Cyclopropane	500	Cyclohexane	260
Cyclopentane	320	Methylcyclohexane	260
Methylcyclopentane	345	1,1-dimethylcyclohexane	250
Ethylcyclopentane	290	Ethylcyclohexane	260
Propylcyclopentane	270	Propylcyclohexane	250
Butylcyclopentane	250	Isopropylcyclohexane	280
Hexylcyclopentane	228	Butylcyclohexane	246
Cycloheptane	280	Isobutylcyclohexane	274
Cyclooctane	275	Tertbutylcyclohexane	342
Cyclododecane	350	Ethylcyclohexane	240
–	–	Octylcyclohexane	235

The rate of auto-ignition, and therefore  $t_{AIT}$ , depends on the number of radicals formed, primarily hydrogen atoms. When the C–H bond is broken, cycloalkyl radicals are formed, which, by eliminating  $\dot{H}$ , are converted into cycloalkenes. Comparing cyclopentane and cyclohexane, the researchers came to the conclusion that for larger cycles this process is much more intense, as a result, the rate of auto-ignition decreases. Substituted cycloalkanes do not form cycloalkenes; when exposed to high temperatures in an oxidizing environment, they break in the substituent chain or in the ring at the C–C bond, which accelerates auto-ignition.

Cycloalkyl radicals form both cycloalkenes and linear structures, further breaking down at the C–C bond. Going through a series of transformations involving radicals, penten-1-yl-5 forms ethene, allylic radical, propene and acrolein, while hexen-1-yl-6 decomposes into allyl, methyl, ethene and propene [14].

Low-temperature oxidation of cycloalkanes, like alkanes, leads to the formation of peroxide structures [15]:



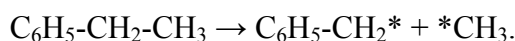
Methyl substituents due to strong C–H bonds either do not change the auto-ignition temperature of cycloalkanes, or contribute to its growth:  $t_{AIT}$  cyclopentane 320 °C, and methylcyclopentane 345 °C; cyclohexane and methylcyclohexane 260 °C. Isomerization of substituents, that is, the formation of structures in which weak  $-\text{CH}_2$  groups are converted into methyl groups, also contributes to an increase in the index:  $t_{AIT}$  of butylcyclohexane 246 °C, and tertbutylcyclohexane 342 °C. An increase in the length of the alkyl side radical leads to a decrease in the indicator (table 1), since in this case, bonds are broken on a less durable linear section of the molecule [3, 12].

The appearance of two double bonds in the cycle, as in linear hydrocarbons, strengthens the molecule:  $t_{AIT}$  cyclohexane 260 °C < cyclohexene 265 °C < cyclohexadiene 360 °C [3, 12].

Aromatic compounds are the most durable structures with the highest auto-ignition temperatures. This is primarily due to the fact that their oxidation forms resonantly stabilized radicals (benzyl, xylil, etc.). Such long-lived radicals are able to recombine, for example, to form diphenylethane, and absorb other free radicals in the system.

The electron-saturated benzene ring promotes the passage of hydrogen substitution reactions in the benzene ring into the  $-\text{CH}_3$  and  $-\text{OH}$  groups, which reduces the number of radicals and slows down the process of auto-ignition [16, 17].

The strongest bonds are C–C and C–H in the benzene ring. Unsubstituted benzene has the highest  $t_{AIT}$ . Due to the elongation of alkyl radicals' chain attached to the ring, oxidation and destruction of the chain with the formation of free radicals takes place primarily in alkyl radicals by the same mechanism as in alkanes. As a result, the longer is the alkyl's side radical in alkylbenzene, the lower is the auto-ignition temperature of the compound. For example, ethylbenzene has the lowest auto-ignition temperature among the  $\text{C}_8\text{H}_{10}$  isomers; when heated, it decays into two radicals by a weak C–C bond:



The C–H bond in the  $-\text{CH}_2$  group is weaker than in  $-\text{CH}_3$ , as a result, rapid accumulation of hydrogen radicals occurs and the auto-ignition temperature decreases (table 2). The ignition time of ethylbenzene is two to three times shorter than that of o-xylene [12, 18].

Table 2

**The auto-ignition temperature of arenes of various structures [3]**

Benzene and arenes containing two or more substituents	Auto-ignition temperature, °C	Monosubstituted and condensed arenes	Auto-ignition temperature, °C
Benzene	560	Methylbenzene	535
1,2-dimethylbenzene	460	Ethylbenzene	430
1,3-dimethylbenzene	530	Propylbenzene	450
1,4-dimethylbenzene	530	Isopropylbenzene	424
1,2,3-trimethylbenzene	480	Butylbenzene	400
1,2,4-trimethylbenzene	500	Secondary butylbenzene	418
1,3,5-trimethylbenzene	550	Isobutylbenzene	430
1,2,4,5-tetramethylbenzene	425	Tertbutylbenzene	450
Pentamethylbenzene	430	Amylbenzene	430
1-methyl-2-ethylbenzene	440	Vinylbenzene	490
1-methyl-3-ethylbenzene	480	Diphenyl	566
1-methyl-4-ethylbenzene	475	Naphthalene	520
1,2-diethylbenzene	395	1-methylnaphthalene	520
1,3-diethylbenzene	450	2-ethylnaphthalene	480
1,4-diethylbenzene	430	Anthracene	470
1-methyl-4-tertbutylbenzene	502	–	–
1,2-diisopropylbenzene	450	–	–
1-methyl-3,5-diethylbenzene	455	–	–
1-methyl-2-vinylbenzene	495	–	–

The auto-ignition temperature of alkylbenzenes with several substituents in the benzene ring is affected by the relative position of the alkyl chain, for example, *o*-xylene has a lower  $t_{AIT}$  than *m*- and *p*-xylenes.

The authors, who studied the auto-ignition behavior of aromatic hydrocarbons note that the low-temperature branching and decrease in  $t_{AIT}$  is due to the proximity and length of the side chains, when hydrogen transfer at the isomerization stage occurs either from an ortho-alkyl group or from another carbon atom of the same alkyl chain. In the absence of such groups, branching follows other paths that require higher energies. Thus, *o*-xylene has the lowest auto-ignition temperature among xylenes, and the ignition time is 20–30 % shorter [18, 19]. The same effect is observed in benzene derivatives with three substituents. 1,2,3-trimethylbenzene, which has two adjacent pairs of substituents has the lowest auto-ignition temperature. In 1,2,4-trimethylbenzene, the radical formed when hydrogen is separated from the methyl group in the fourth position, contributes, like benzyl, to chain breakage. As a result, only 67 % of 1,2,4-trimethylbenzene radicals lead to further chain growth, whereas in *o*-xylene this indicator is close to 100 %. 1,3,5-trimethylbenzene has the strongest structure of trimethylbenzenes, its auto-ignition temperature is higher than that of toluene (table. 2) [16, 18, 20].

The auto-ignition temperature of condensed arenes decreases with an increase in the number of benzene rings in the molecule: anthracene < naphthalene < benzene (table 2). Methyl substituents in condensed structures, as in benzene derivatives, do not affect the resistance of the molecule. The auto-ignition temperature of naphthalene and methylnaphthalene is 520 °C, with the elongation of the chain of the alkyl substituent  $t_{AITi}$  decreases (table 2).

The presence of a double bond in the substituent contributes to an increase in the auto-ignition temperature: ethylbenzene 430 °C < vinylbenzene 490 °C, 1-methyl-2-ethylbenzene 440 °C < 1-methyl-2-vinylbenzene 495 °C, which is explained by the conjugation effect: the double bond  $\pi$ -electrons are conjugated with the benzene ring  $\pi$ -electronic system. As a result, the molecule is getting stronger and the auto-ignition temperature increases. It should be noted that this effect of conjugation of a substituent and the benzene ring will be characteristic only for vinyl radicals or substituents by the type of conjugated dienes.

## Conclusion

The existing methods for calculating the auto-ignition temperature do not provide the required accuracy, the determination of the indicator in laboratory conditions is not always possible and heavily depends on the experimental conditions, as a result, the theoretical data on  $t_{AIT}$  for the same substance may differ significantly [12]. The creation of a database of auto-ignition temperatures defined by GOST for substances of various structures and an understanding of the kinetics of auto-ignition chemical processes will allow specialists to pre-assess the fire hazard of cyclic hydrocarbons by comparing them with known substances of similar structure, conclude on the applicability of the calculation results according to the proposed methods and make a forecast of the indicator.

When assessing the fire hazard of cyclic hydrocarbons, it should be borne in mind that the most stable are unsubstituted cycles or cycles containing methyl groups or branched alkyl substituents with a large number of methyl groups as substituents. An elongation of the substituent leads to a decrease in the auto-ignition temperature due to the appearance of weak C–C bonds in the linear chain.

Substituents that are ortho-positioned to each other reduce the auto-ignition temperature. The appearance of double bonds in the nonaromatic cycle or in the structure of the substituent contributes to an increase in  $t_{AIT}$ , if this creates conditions for the  $\pi$ -electrons conjugation of the substituent and the benzene ring.

Polycyclic aromatic structures have a lower auto-ignition temperature than benzene derivatives.

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