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Inhibition–initiation in the pyrolysis of hydrocarbon mixtures

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ABSTRACT. The results of investigations on the mutual influence of hydrocarbons of various classes on the rate and route of decomposition under copyrolysis conditions are correlated and discussed. A general concept has been formulated as to the mechanism of the inhibition–initiation phenomenon based on competing chain propagation reactions according to which a hydrocarbon may act both as an inhibitor and as an initiator of decomposition. The course of this action is determined by the character of partner behaviour and by the concentration of reactive radicals.

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I. Introduction

The pyrolysis of hydrocarbons lies at the basis of the manufacture of fundamental products such as monomers and starting materials for fine organic synthesis in the chemical and petrochemical industries. The traditional raw material for pyrolysis is gas condensate and directly distilled solvent naphtha consisting mainly of alkanes, naphthenic hydrocarbons and a small quantity of aromatics. The involvement of gas oil and residual fractions after oil refining, of coal liquefaction products, carrying out the process under conditions of recirculation of short chain fractions separated from the products and also the preliminary treatment of a raw material by hydrogenation or hydrocatalytic treatment, complicates the composition of the raw material even more and demands consideration of the mutual influence of the components of the reaction mixture on the pattern of their thermal decomposition. This is also important because in addition to the initial hydrocarbons the products of their pyrolysis (hydrogen, methane, alkenes, aromatic hydrocarbons) are always present in the reaction zone.

The first investigations of the effect of added unsaturated hydrocarbons on the thermal decomposition of alkanes appeared in the thirties. With the development of industrial processes interest in the mutual effect grew further. This was particularly so in connection with the development of kinetic models of pyrolysis for which information is needed on the detailed mechanism of the decomposition of individual hydrocarbons and mixtures of them. Up to the present many experimental data have been accumulated on the behaviour of mixtures of hydrocarbons of different classes during pyrolysis. However the results and their interpretation by various authors are frequently in conflict.

The aim of the proposed review is to discuss the results of investigations of the thermal decomposition of mixtures of hydrocarbons and to formulate a general concept for the overall mechanism of their mutual effect as a system of competing reactions of radicals (intermediates) of various types propagating the chain. The pyrolysis considered is mainly of model binary mixtures of hydrocarbons present in the raw material or formed under the conditions of an industrial process.

II. Pyrolysis of mixtures of alkanes and alkenes

The pyrolysis of mixtures of alkanes with propene and 2-methylpropene, which are classic inhibitors of the process, has been investigated most. In the earlier work the overall kinetics of the process were generally studied by the change in pressure in the system. In this way no attention was paid to the conversion of the actual inhibitor,[1–4] assuming for example that it polymerised.[4] Attempts to assess the influence of ethane on the rate of decomposition of propene[5] and the development of these investigations[6–9,11] enabled exhaustive results to be obtained on the effect of an alkane on the decomposition of propene and 2-methylbutene at 700–900 °C. The investigations were carried out using propene labelled with radioactive carbon ^{14}C which enabled the course and rate of disappearance of even very small additions of propene to be followed. It was established as a result that ethane and propane show an initiating action on the decomposition of propene in its inhibition of alkane pyrolysis.

The rate constant for the decomposition of propene ($k_{C_3H_6}$) initiated by ethane is sharply reduced when the content of ethane in the initial mixture is reduced. Thus in a mixture with 99.9 vol.% ethane the rate constant for the decomposition of propene was approximately two orders of magnitude greater than the rate constant for the decomposition of pure propene. At the same time the rate constants for the decomposition of pure propene and for its equimolar mixture with ethane were practically equal.[7]

A smoother dependence of the rate constant for the decomposition of propene on propane concentration in the initial mixture was observed in the case of mixtures of propane with propene. Even in a mixture containing about 32 vol.% propane at a

temperature of 850 °C the rate constant for the decomposition of propene was approximately 5 times greater.[9] A further increase in the propane concentration in the mixture is accompanied by a proportionate increase in the rate constant for propene decomposition. The mutual effect of propane and propene on pyrolysis of their mixtures was first noticed in a study[12] in which it was shown that at 900 °C and atmospheric pressure the rate constant for propane decomposition ($k_{C_3H_8}$) fell sharply when the propene content in the initial mixture was increased and $k_{C_3H_6}$ increased with increase in propane concentration.

The yield of the main products from the pyrolysis of ethane and propane mixed with C_3H_6 differed from that calculated using the additivity hypothesis for their formation.[6–10,13] Thus a six-fold increase in the yield of 1-butene was recorded in the pyrolysis of a mixture of propane with propene.[13]

From the character of the change in overall rate constants for the decomposition of hydrocarbons[10,11] it was established that 2-methylpropene also shows an inhibitory action on the decomposition of C_2-C_4 alkanes. The rate of decomposition of 2-methylpropene in the mixtures increases with an increase in alkane content. However the inhibitory action of propene on the decomposition of ethane and propane is stronger than that of 2-methylpropene. The rate constants for the decomposition of propane in the presence of 20 vol.% propene and 2-methylpropene at 850 °C are 25 and 33 s^{-1} respectively.[10]

In the case of n-butane both C_3H_6 and iso-C_4H_8 show a less strong and approximately identical inhibitory action. At 850 °C the rate constants for the decomposition of n-butane in the presence of 20 vol.% propene and 2-methylpropene are about 90 and 95 s^{-1} respectively.[11]

In its turn n-butane shows the strongest initiating action on the decomposition of an inhibitor among the alkanes considered above. Thus at 800 °C the rate constants for the decomposition of iso-C_4H_8 in equimolar binary mixtures with ethane, propane and n-butane are about 2, 8 and 17 s^{-1} respectively.[10]

The yield of pyrolysis products of mixtures of alkanes with 2-methylpropene also differed from additivity and the greatest deviation from that calculated was observed on pyrolysis of mixtures of ethane with 2-methylpropane and of propane with propene.

An inhibitory action of propene and 2-methylpropene on the overall decomposition process of the higher n-alkanes ($>C_5$) has been recorded. At relatively low temperatures (450–540 °C) propene and 2-methylpropene inhibit the decomposition of pentanes,[14–16] and 2-methylpropene is a stronger inhibitor than propene. The accelerating action of the pentanes and of n-hexane on the decomposition of the inhibitors has also been established.[17]

According to other data[18,19] propene and 2-methylpropene act both as inhibitors and as initiators of the thermal decomposition of n-hexane. At 545 °C small additions (up to 4 vol.%) of propene inhibit the decomposition of n-hexane. Limitation of the decomposition rate for n-hexane was observed with an increase in the propene concentration. At higher temperatures (570 and 595 °C) on the other hand addition of propene shows an initiating action on n-hexane decomposition. The inhibitory action of 2-methylpropene on the decomposition of n-hexane weakens even at a concentration of about 2 vol.% and is transformed into an initiating action on increasing it further.[19] The dual action of additions of propene on the decomposition of propane was established in more recent work by the same authors.[20] A transition from an inhibitory to an initiating action was detected above 580 °C. An increase in the yield of methane and ethylene was recorded during this.

The conclusions are far more ambiguous concerning the action of additions of other alkenes (ethylene, 1-butene, 2-butene and larger) to the decomposition of alkanes. The inhibitory action of these alkenes on the decomposition of various alkanes is recorded in several studies. For example ethylene and 2-butene inhibit the decomposition of propane at 445–575 °C.[21] Ethylene, propene, *trans*-2-butene and 2-methyl-2-butene are inhibitors of the decomposition of isobutane at 470–510 °C.[22] Propene, 2-methylpropene and 2-methyl-2-butene show an inhibitory action on the decomposition of 2,2-dimethylbutane at 450 °C.[22]

Inhibition of the decomposition of n-nonane by 2-pentene at 725 °C has been reported.[23] The rate constant for the decomposition of n-nonane on pyrolysis was reduced by approximately 34% on admixture with 2-pentene. The rate constant for the decomposition of 2-pentene was practically unchanged by this but the activation energy of the process was increased.

According to other data[1] ethylene, n-butene and 2,2,4-trimethylpentene do not show a marked inhibitory action on the decomposition of iso-octane (2,2,4-trimethylpentane) at 550 °C. No mutual effect on the rate and course of the decomposition was detected in the copyrolysis of ethane with ethylene in the temperature range 800–900 °C.[24] The same result was obtained when investigating the pyrolysis of mixtures of ethane with ethylene at a lower temperature (770 °C).[25] The addition of butenes (1-butene and 2-butene) also did not change the rate of decomposition of propane and n-butane at 590–635 °C, however they inhibited the decomposition of ethane.[26] The inhibition in the case of ethane is explained by the formation of propene from the butenes. Propene is one of the main decomposition products of propane and butane and consequently some increase in its yield at the expense of the butenes does not have an appreciable effect on the overall rate of the process.

However when investigating the pyrolysis of ethane with small additions of 1-butene labelled with radioactive carbon ^{14}C, no effect of the alkene on the decomposition of ethane was detected at higher temperatures (750–930 °C).[27] In this case a weak initiating action of ethane on the decomposition of 1-butene appeared; this was traced particularly clearly in mixtures with a small addition of 1-butene (0.2 vol.%). The weak initiating action of the C_5-C_7 n-alkanes on the decomposition of 1-alkenes with 6–8 carbon atoms at 600–800 °C was also recorded.[28] In this study, the overall rate constants for the decomposition of the n-alkanes were practically unchanged. The yield of hydrogen and methane was different from the additive value, but the yields of ethylene and propene were close to the calculated values. The initiating action of the thermally more stable ethylene on the decomposition of n-hexane on copyrolysis at 800 °C has been demonstrated.[29] In truth these authors also recorded that the conversion of n-hexane was also increased in the presence of ethylene. The decomposition of n-hexane initiated by 1-hexene has also been observed at 650–690 °C.[30]

III. Pyrolysis of mixtures of alkanes and dienes

1,3-Butadiene, 2-methyl-1,3-butadiene and 1,3-pentadiene display an inhibitory effect on the decomposition of alkanes[1,31–33] which was demonstrated by experiments with radioactive (^{14}C) ethane and 1,3-butadiene.[31] The extent of conversion of ethane falls with an increase in the concentration of 1,3-butadiene in the initial mixture reaching a minimum at an approximately equimolar mixture of ethane and 1,3-butadiene, which at 800 °C was 2.8 times lower than

the degree of conversion of pure ethane. In this, ethane shows an initiating action on the decomposition of 1,3-butadiene. At 800 °C the conversion of 1,3-butadiene in mixtures containing about 99 vol.% ethane was 1.8 times higher than in pure 1,3-butadiene. The content of the main pyrolysis products of mixtures of ethane with 1,3-butadiene (H_2, CH_4, C_2H_4) did not change linearly with the change in composition of the mixture, which indicates the non-additive nature of their formation.

1,3-Pentadiene inhibits the decomposition of propane but propane shows an initiating action on the conversion of 1,3-pentadiene at 730–880 °C.[32] At 780 °C the overall rate constant for the decomposition of 1,3-pentadiene in mixtures with propane (90 vol.% C_3H_8) was increased approximately five-fold. An appreciable increase in the yield of 1,3-butadiene and a fall in the yield of cyclopentadiene was observed during this. The decomposition of propane slowed with an increase in the 1,3-pentadiene added to the initial mixture.

1,3-Butadiene and 2-methyl-1,3-butadiene show a strong inhibitory action on the decomposition of octanes at 550 °C.[1,33]

On the other hand allene initiates the thermal decomposition of n-alkanes.[34–36] Small additions of allene (0.23 wt.%) strongly accelerate the decomposition of n-hexane in the temperature range 630–690 °C.[34] At 630 °C the extent of decomposition of 0.23 wt.% allene was 2.5 and 23.0% respectively. The composition of the products was unchanged. Small additions of allene (0.42 mol%) also accelerate the decomposition of ethane in the temperature range 800–860 °C.[36] However the initiating action of allene in the decomposition of ethane was far weaker than in the decomposition of n-hexane[34] and n-hexadecane.[35] At temperatures of 800, 835 and 860 °C the ratio of the rate constants for the decomposition of ethane mixed with allene and of pure ethane were 1.43, 1.40 and 1.25 respectively.

IV. Pyrolysis of mixtures of alkanes

The investigations of the pyrolysis of mixtures of alkanes refer mainly to mixtures of the gaseous C_2–C_4 hydrocarbons. The majority of the studies report weak, sometimes contradictory, mutual effects of alkanes on the rate and course of decomposition on pyrolysis of mixtures of them. The absence of a mutual effect is characteristic for mixtures of alkanes with similar thermal stabilities. No change in rate constant was detected for the decomposition by combined pyrolysis for ethane and propane.[37,38] On the other hand an increase in the rate constant for the decomposition of propane in the presence of ethane and a reduction in the rate constant for the decomposition of ethane was recorded,[39] although the conversion of ethane was increased and the conversion of propane was reduced at 760–925 °C and on dilution with nitrogen.[40–42] According to other data[43] the rate of decomposition of propane was higher at 750 °C but at 800 °C it was comparable with the rate of decomposition of pure propane. However at 750 °C no change was observed in the rate of decomposition of ethane in mixtures but at 800 °C it was less than in the case of pure ethane. In this case and in another study[39] the yield of ethylene may be calculated from the hypothesis of the additivity of its formation. In addition there are reports on higher[41,42,44,45] (than additive) and lower[46] yields of ethylene on pyrolysis of these mixtures.

The difference in the data on the selectivity of C_2H_4 formation must also be noted. In some cases a lower[44] and in others a higher[6,47] selectivity of C_2H_4 formation was indicated,

The results of investigations on the mutual effect of ethane and n- and isobutane are also ambiguous.[37–40,48–52] Both an initiating action of n- and isobutane on the decomposition of ethane[48,50,51] and a strong inhibition of C_2H_6 decomposition by n-butane[49] have been recorded. Small additions of the butanes initiate the decomposition of C_2H_6 without an appreciable change in the distribution of products but larger additions (> 25%) inhibit.[50]

The results of investigations on the pyrolysis of mixtures of C_2H_6 with larger alkanes are also inconsistent. At 800 °C, atmospheric pressure and carrying out the process in a fluidised bed of quartz sand, additions of n-heptane and n-octane initiate the pyrolysis of ethane.[51] The initiating action is strengthened with an increase in the n-alkane content in the mixture and n-octane is a stronger initiator. The initiating action of the n-alkanes on the decomposition of ethane increased in the series n-C_4H_{10} > n-C_7H_{16} > n-C_8H_{18}. A deviation in the yield of the main products from that calculated using the additivity hypothesis (particularly in the case of additions of n-octane) was noted which was expressed particularly in the increase in the yields of C_2H_4 and C_3H_6 and a reduction in the yield of hydrogen.

At the same time an inhibitory action of small additions of mixtures of C_{11}–C_{14} n-alkanes on the decomposition of ethane has been reported.[52] This seems even more unlikely since the same additions show an initiating action on the decomposition of propane. In both cases a change in the distribution of products was recorded which was manifestly greater in mixtures with propane.

On pyrolysis of binary mixtures of propane with isobutane and neopentane at 650–690 °C and a molar ratio of components of 0.5 and 1 an initiating action was established for isobutane on the decomposition of propane which was strengthened by an increase in the isobutane content of the mixture.[37] Propane inhibits the decomposition of isobutane to an insignificant extent. However this effect does not depend on the quantity of propane added. In the pyrolysis of binary mixtures of neopentane with propane and isobutane an initiating action was recorded for neopentane (which was stronger for mixtures with propane).

In the case of the thermal decomposition of mixtures of propane with isobutane of varied composition and also of equimolar mixtures of isobutane with neopentane at higher temperatures (700–850 °C) isobutane also initiates the decomposition of propane which like ethane (but to a lesser extent), shows an inhibitory action on the pyrolysis of isobutane.[48] The distribution of the products differed from that expected from additivity. In equimolar mixtures of isobutane with neopentane the mutual effect of the hydrocarbons on the rate and course of decomposition was almost not apparent.

The pyrolysis of mixtures of n- and isobutane was characterised by the insignificant initiating action of isobutane over a wide temperature range, viz. 650–690 °C,[37] 640–790 °C,[53] 575–850 °C.[40] n-Butane shows a weak inhibitory effect. The observed distribution of products differed from that calculated from the additivity hypothesis for their formation. Thus on pyrolysis of an equimolar mixture of n- and isobutane at 660 °C the rate of decomposition of isobutane was reduced and of n-butane increased 1.1 and 1.4 times respectively.[37] On increasing the temperature in the range 575–850 °C the mutual effect is strengthened.[40] At the same time it was recorded that in equimolar mixtures of n- and isobutane the mutual effect of the butanes on the rate and course of the decomposition was almost invisible at 700–850 °C.[48]

An insignificant mutual effect on the rate of decomposition was recorded in the pyrolysis (600–790 °C) of a mixture of n-heptane and iso-octane of composition close to equimolar. n-Heptane retards the decomposition of iso-octane to an insignificant extent and, in its turn, iso-octane accelerates insignificantly the pyrolysis of n-heptane. The distribution of the products follows the additivity principle in cases of low conversion but deviates somewhat from it on extended conversion.[54,55] In general, no changes were detected in the distribution of products and conversion on pyrolysis of mixtures of n-nonane and n-octane at 650–725 °C.[23]

On pyrolysis of mixtures of alkanes the mutual effect of the hydrocarbons on the rate and course of the decomposition is weak and the character of this effect is determined by the experimental conditions (temperature, pressure, mixture composition). The data considered above are summarised for clarity with the experimental conditions in Table 1.

Table 1. Mutual effects on the decomposition rate on pyrolysis of binary mixtures of C_2–C_9 alkanes.

Mixture	Content of second component in mixture, %	Temperature, °C	Total pressure, atm	Type of action of components	Ref.
$\frac{C_2H_6}{C_3H_8}$	25–75	850–875	1.4–2.0	Initiator Inhibitor	[40]
$\frac{C_2H_6}{C_3H_8}$	1–77	807–923	0.9–2.0	No effect	[38]
$\frac{C_2H_6}{C_3H_8}$	0–100	759–925	1.1–1.3	Inhibitor Initiator	[42]
$\frac{C_2H_6}{C_3H_8}$	15.5; 50; 70	750	1	Initiator No effect	[43]
$\frac{C_2H_6}{C_3H_8}$	12.5; 50; 70	800	1	No effect Inhibitor	[43]
$\frac{C_2H_6}{C_3H_8}$	50	690	1	No effect	[37]
$\frac{C_2H_6}{C_3H_8}$	25; 50; 75	650–870	1.2–2.3	Initiator Inhibitor	[39]
$\frac{C_2H_6}{n-C_4H_{10}}$	25–75	575–850	1.4–2.0	Strong initiator Strong inhibitor	[40]
$\frac{C_2H_6}{n-C_4H_{10}}$	<25	700–850	–	– Initiator	[50]
$\frac{C_2H_6}{n-C_4H_{10}}$	>25	700–850	–	– Inhibitor	[50]
$\frac{C_2H_6}{n-C_4H_{10}}$	–	700–900	0.9–2	No effect	[38]
$\frac{C_2H_6}{n-C_4H_{10}}$	12.7–82.2	800	1	– Initiator	[51]
$\frac{C_2H_6}{iso-C_4H_{10}}$	14.1; 29.5; 51.5	755–856	0.13	Inhibitor Initiator	[48]
$\frac{C_2H_6}{iso-C_4H_{10}}$	<25	700–850	–	– Initiator	[50]
$\frac{C_2H_6}{iso-C_4H_{10}}$	>25	700–850	–	– Inhibitor	[50]
$\frac{C_2H_6}{iso-C_4H_{10}}$		700–900	0.9–2.0	No effect	[38]
$\frac{C_2H_6}{n-C_7H_{16}}$	52.4–81.5	800	1	– Initiator	[51]
$\frac{C_2H_6}{n-C_8H_{18}}$	60.0–89.1	800	1	– Initator	[51]
$\frac{C_3H_8}{n-C_4H_{10}}$	25.5; 50; 75	575–850	1.4–2.0	Weak inhibitor Weak inhibitor	[40]
$\frac{C_3H_8}{iso-C_4H_{10}}$	33.3; 50	650–690	1	Weak effect Strong initiator	[37]
$\frac{C_3H_8}{iso-C_4H_{10}}$	50	651	1	Weak inhibitor Strong initiator	[37]
$\frac{C_3H_8}{iso-C_4H_{10}}$	50	686	1	Weak initiator Strong initiator	[37]
$\frac{C_3H_8}{iso-C_4H_{10}}$	50	660	1	Weak initiator Strong initiator	[37]
$\frac{C_3H_8}{iso-C_4H_{10}}$	33.3	660	1	No effect Strong initiator	[37]
$\frac{C_3H_8}{iso-C_4H_{10}}$	50.4; 86.2	749–855	0.13	Inhibitor Initiator	[48]
$\frac{C_3H_8}{iso-C_4H_{10}}$	~10	749–855	0.13	Weak inhibitor No effect	[48]
$\frac{C_3H_8}{\text{neopentane}}$	50	660	1	Weak initiator Very strong initiator	[37]
$\frac{n-C_4H_{10}}{iso-C_4H_{10}}$	50	660	1	Weak inhibitor Initiator	[37]
$\frac{n-C_4H_{10}}{iso-C_4H_{10}}$	25; 50; 75	575–850	1.4–2.0	Weak inhibitor Weak initiator	[40]
$\frac{n-C_4H_{10}}{iso-C_4H_{10}}$	50	735–845	0.13	Practically no effect	[48]
$\frac{n-C_4H_{10}}{iso-C_4H_{10}}$	–	807–927	1–1.7	No effect	[38]
$\frac{iso-C_4H_{10}}{\text{neopentane}}$	50	721–860	0.13	Practically no effect	[48]
$\frac{iso-C_4H_{10}}{\text{neopentane}}$	50	660	1	No effect Initiator	[37]
$\frac{n-\text{heptane}}{iso-\text{octane}}$	~50	660–790	1	Weak inhibitor Weak initiator	[54, 55]
$\frac{n-\text{octane}}{n-\text{nonane}}$	25; 48; 75	650–725	1	No effect	[23]

V. Pyrolysis of alkanes and cycloalkanes

The few investigations on the pyrolysis of alkanes in mixtures with cycloalkanes indicate unambiguously the initiating action of alkanes on the decomposition of cycloalkanes.

Ethane and n-pentane initiate the decomposition of cyclopentane at 800–870 °C, n-pentane showing the stronger initiating action.[56]

On pyrolysis of cyclohexane in the presence of ethane, propane[57,58] and n-hexane[59] (725–900 °C) the initiating action of the alkanes was manifest most strongly in mixtures with a small cyclohexane content (10–15%). The conversion of alkanes falls sharply on increasing the cyclohexane content of the mixture. The extent of conversion of ethane was reduced to a minimum value in mixtures containing 10–15 vol.% cyclohexane.

Propane and n-hexane show approximately the same initiating action on the decomposition of cyclohexane. Ethane is a less strong initiator. An appreciable deviation is observed in all cases in the yield of the main products from that calculated from the additivity hypothesis. This was particularly strongly shown for hydrogen, methane, ethylene, and propene.

n-Heptane and iso-octane also show an initiating action on the decomposition of cyclohexane over a wide temperature range (600–850 °C).[54,55] n-Heptane is a strong initiator of the pyrolysis of cyclohexane compared with iso-octane, the accelerating action of which on cyclohexane decomposition is insignificant at 600–790 °C.[54] An appreciable deviation from additivity of the yields of main products from the pyrolysis of the mixtures was recorded in cases of extended conversion.[55] For low conversion the yields of pyrolysis products from mixtures of n-heptane with cyclohexane and of iso-octane with cyclohexane may be calculated by the additivity hypothesis.

Similarly, n-heptane inhibits the decomposition of methylcyclohexane (680 °C) but the latter shows an insignificant inhibitory action on the breakdown of n-heptane.[60]

An inhibition–initiation effect was also recorded in an investigation of the pyrolysis of mixtures of decalin with n-decane at 685–760 °C [61] and with n-dodecane at 480–525 °C.[62] The initiation effect appeared more clearly in mixures of decalin with n-decane while the inhibitory action of decalin is more marked on copyrolysis of decalin with n-dodecane. A deviation of the product distribution from that calculated from additivity of the thermal decomposition of the hydrocarbons in the mixtures was noted.[62]

VI. Effect of aromatic hydrocarbons

There are practically no literature data on the effect of aromatic hydrocarbons on the decomposition of hydrocarbons of other classes.† Only the inhibitory action of the polycyclic hydrocarbons naphthalene and phenanthrene on the decomposition of n-hexadecane and decalin on combined pyrolysis of binary mixtures of cycloalkanes and aromatic hydrocarbons in the temperature range 800–900 °C have been recorded.[63] It was shown that the inhibitory action of the aromatic hydrocarbons was more strongly developed in the pyrolysis of decalin than of n-hexadecane.

† The toluene and xylene procedures for investigating thermal decomposition under conditions of inhibiting the radical process are not considered in the present review.

The lighter alkanes (methane, ethane, propane, butane) initiate the decomposition of toluene at 800–1200 °C.[64] In the presence of CH_4, C_3H_8 and butanes, which generate methyl radicals, the yield of ethylbenzene and styrene are increased. Ethane affects the yield of ethylbenzene to a lesser extent but it enables an increase in the yield of n-propylbenzene to be achieved.

The initiating action of 1-hexene on the decomposition of toluene takes place at 630–720 °C.[30] Initiation of the decomposition of benzene by toluene was also noted.

VII. Mechanism of inhibition–initiation in the pyrolysis of hydrocarbon mixtures

The theory of the radical–chain decomposition of n-alkanes, developed initially in the thirties by Rice[65,66] and refined by him with Kossiakoff,[67] has been applied successfully to the description of thermal conversions of hydrocarbons of other classes, particularly alkenes,[68] cycloalkanes[57,69] and aromatic hydrocarbons.[70]

The radical–chain mechanism comprises three stages. The first is chain formation by fission of the weakest bond in the hydrocarbon molecule, then chain propagation and a termination stage by recombination and disproportionation of the radicals propagating the chain. The chain propagation (or development) stage comprises the reaction of the radicals propagating the chain (β-radicals) with a molecule of the initial hydrocarbon (abstraction of a H atom or addition at a double bond), and also β-decomposition and isomerisation of the resulting heavy radicals (μ-radicals).

This concept is the basis of the formal kinetics of the pyrolysis process.[71] A particularly important role is played here by reactions leading to the formation and disappearance of β-radicals which are responsible for the yield of the main products. On carrying out the process in the presence of other compounds the latter are also involved in reaction with the β-radicals. In addition the β-radicals react with the pyrolysis products and this becomes important at greater convesions. The rate of carrying out these processes and the probability of regenerating β-radicals is reflected both in the distribution of products and in the rate of the overall process.

1. Early ideas on the mechanism of inhibition

a) Addition of β-radicals to a double bond

The retardation of the thermal decomposition of n-alkanes by the products formed and also by addition of alkenes was first established by Dintses and Frost.[72] During the pyrolysis of a n-alkane the β-radicals add to the double bond of an alkene with the formation of unreactive radicals,[73] such as

$$R + C_3H_6 \longrightarrow CH_3-\underset{\displaystyle R}{\underset{|}{CH}}-\dot{C}H_2,$$

$$R + C_3H_6 \longrightarrow CH_3-\dot{C}H-CH_2-R,$$

which leads to chain termination and a reduction in the decomposition rate of the alkane. These ideas were used to explain the effect of some unsaturated hydrocarbons (propene, 2-methyl-1,3-butadiene, 2-methylpropene, 1,3-butadiene, butene, 2,2,4-trimethylpentene) on the decomposition of iso-octane.[1] The unsaturated hydrocarbons investigated may be arranged in the following series according to their efficiency of inhibitory action.

$$C_4H_6 > C_3H_6 > \text{2-methyl-1,3-butadiene} > \text{2-methylpropene}$$

Butene and 2,2,4-trimethylpentene do not inhibit the decomposition of iso-octane since they do not form inactive radicals on reaction with β-radicals. The addition of methyl radicals to 2-methyl-1,3-butadiene does not lead to the formation of stable unreactive radicals, consequently its inhibitory action is weaker than the action of propene and 1,3-butadiene. 2-Methylpropene, having only one double bond in the molecule, is a weaker inhibitor than 2-methyl-1,3-butadiene. As a rule, addition of the ethyl radical at the double bond of an inhibitor does not lead to the formation of a stable unreactive radical consequently reactions involving the ethyl radical are not considered in the mechanism of inhibition (addition reactions of H atoms are not taken into account).

b) The formation of low reactivity allyl radicals in reactions of H atom extraction

A mechanism for the inhibition of alkane decomposition by certain alkenes (C_3H_6, iso-C_4H_8) was considered in studies by Stepukhovich and collaborators,[3,74] Leidler and collaborators,[4] in the early work, of Niclause and collaborators[16] and by several other authors.[4,75–77] This is based on the occurrence of a reaction involving abstraction of hydrogen atoms from the inhibitor by the reactive radicals propagating the chain with the formation of radicals of an allylic type which do not participate in chain propagation reactions, such as

$$R(\dot{H},\ \dot{C}H_3) + C_3H_6 \longrightarrow C_3H_5 + RH. \qquad (1)$$

In fact, in recent studies by Stepukhovich a kinetic scheme is proposed for alkane decomposition retarded by additions of inhibitors (C_3H_6) which includes a chain propagation reaction involving an allyl radical.[19]

$$M \longrightarrow 2R + 2M^1,$$

$$R + M \longrightarrow RH + mM^1 + R,$$

$$R + I \longrightarrow RH + R^1,$$

$$R^1 + M \longrightarrow R^1H + mM^1 + R,$$

$$R + \text{walls} \rightarrow \text{products},$$

$$R^1 + \text{walls} \rightarrow \text{products},$$

where M and M_1 are molecules of alkane and alkene, R and R^1 are alkyl and allyl radicals respectively, and I is the inhibitor molecule.

Inhibition is effected by the reduction in the rate of the chain propagation reaction by the participation of the less reactive allyl radicals.

2. Mechanism of inhibition–initiation on pyrolysis of mixtures of hydrocarbons

a) Inhibition–initiation on joint pyrolysis of alkanes with low molecular alkenes

A drawback of the schemes give above is the lack of data characterising the kinetics of decomposition of the inhibitor itself under conditions of joint pyrolysis.

This is linked with the fact that, as a rule, the inhibitor or its decomposition products are no different from the decomposition products of the alkanes themselves. Consequently only the use of special methods of investigation enables the decomposition of the inhibitor on pyrolysis of mixtures to be followed. The method of introducing a labelled inhibitor is the most suitable for this.

Detailed investigations on the pyrolysis of ethane and propane with added propene labelled with radioactive carbon (^{14}C) have enabled the course of the conversion of propene on pyrolysis in mixtures to be traced and the effect of the alkane on the rate and course of its decomposition to be assessed.[6,9,78] It was established that the alkane shows an initiating action on the conversion of propene which is stronger for increased alkane concentration in the mixture (Fig. 1). It is therefore possible to speak of the phenomenon of a simultaneous inhibition–initiation in the pyrolysis of alkanes with propene. A mechanism is proposed to describe this phenomenon, which includes the replacement (with the participation of propene) of the hydrogen atoms most reactive in the chain propagation reaction by less reactive methyl radicals. This is effected through successive stages in the addition of H atoms to propene with the formation of an excited propyl radical and its subsequent breakdown:

$$\dot{H} + C_3H_6 \rightleftharpoons [(CH_2CH_2CH_3)^{\cdot}]^* \longrightarrow CH_3^{\cdot} + C_2H_4. \qquad (2)$$

This leads, on the one hand, to inhibition by propene of the decomposition of the alkanes and, on the other, to initiation of the conversion of propene by hydrogen atoms generated on decomposition of the alkane.

It was established from the data on the distribution of radioactivity in the pyrolysis products, when investigating the pyrolysis of ethane with added propene labelled with ^{14}C at the centre carbon atom ($H_2C=^{14}CH-CH_3$), that up to 95% propene was consumed in the formation of ethylene[6] and only 5% went to the formation of other products.

$$R + C_3H_6 \longrightarrow RH + \dot{C}_3H_5,$$

$$\dot{C}_3H_5 \longrightarrow C_3H_4 + \dot{H}, \qquad (3a)$$

$$\dot{C}_3H_5 \longrightarrow C_2H_2 + CH_3^{\cdot}, \qquad (3b)$$

$$R = \dot{H}, CH_3^{\cdot}.$$

In the pyrolysis of propane mixed with radioactive propene the selectivity of forming C_2H_4 is lower and is reduced on increasing the propene concentration in the initial mixture but the selectivity of forming the remaining products was increased. At 850 °C and an extent of conversion of radioactive propene of about 40%, the selectivity of forming radioactive ethylene was 70, 65, 52 and 22.5% at propene contents in the initial mixture of 1.77, 6.41, 30.78 and 68.18 vol.% respectively.[9] It follows from this that reaction (2) is not the sole route for the conversion of propene in this case. In fact on pyrolysis of mixtures of ethane with propene the overall decomposition rate of radioactive propene coincides with the rate of accumulation of radioactive ethylene and on pyrolysis of mixtures of propane with propene the overall decomposition rate of radioactive propene is appreciably higher than the rate of formation of radioactive ethylene (see Fig. 1).

Consequently when describing the decomposition of ethane in the presence of small additions of propene (up to 10 vol.%) it is possible to consider just one route for the conversion of propene by reaction (2).

$$C_2H_6 \rightleftharpoons 2CH_3^{\cdot}, \quad (4)$$

$$CH_3^{\cdot} + C_2H_6 \longrightarrow CH_4 + C_2H_5^{\cdot},$$

$$C_2H_5^{\cdot} \longrightarrow C_2H_4 + H^{\cdot},$$

$$H^{\cdot} + C_2H_6 \longrightarrow H_2 + C_2H_5^{\cdot}, \quad (5)$$

$$H^{\cdot} + C_3H_6 \longrightarrow CH_3^{\cdot} + C_2H_4, \quad (2)$$

$$CH_3^{\cdot} + C_2H_5^{\cdot} \longrightarrow C_3H_8,$$

$$2C_2H_5^{\cdot} \longrightarrow C_4H_{10}.$$

In the pyrolysis of propane with even small additions of propene it is necessary to consider routes in addition to reaction (2) for the decomposition of C_3H_6. The main route at high temperatures (> 800 °C) is that leading to the formation of acetylene and C_3H_4 hydrocarbons [reactions (1) and (3)]:

$$C_3H_8 \rightleftharpoons CH_3^{\cdot} + C_2H_5^{\cdot},$$

$$C_2H_5^{\cdot} \longrightarrow C_2H_4 + H^{\cdot},$$

$$R(\dot{H}, \dot{C}H_3) + C_3H_8 \rightarrow RH + pr\text{-}C_3H_7^{\cdot},$$

$$R(\dot{H}, \dot{C}H_3) + C_3H_8 \rightarrow RH + sec\text{-}C_3H_7^{\cdot},$$

$$pr\text{-}C_3H_7^{\cdot} \rightarrow C_2H_4 + CH_3^{\cdot},$$

$$sec\text{-}C_3H_7^{\cdot} \rightarrow C_3H_6 + H^{\cdot},$$

$$H + C_3H_6 \longrightarrow C_2H_4 + CH_3^{\cdot}, \quad (2)$$

$$H + C_3H_6 \longrightarrow C_3H_5^{\cdot} + H_2, \quad (1a)$$

$$CH_3^{\cdot} + C_3H_6 \longrightarrow C_3H_5^{\cdot} + CH_4, \quad (1b)$$

$$C_3H_5^{\cdot} \longrightarrow C_3H_4 + H, \quad (3a)$$

$$C_3H_5^{\cdot} \longrightarrow C_2H_2 + CH_3^{\cdot}, \quad (3b)$$

$$CH_3^{\cdot} + C_3H_5^{\cdot} \longrightarrow C_4H_8,$$

$$2C_2H_5^{\cdot} \longrightarrow C_4H_{10}.$$

The fairly marked contribution of reaction (1) on pyrolysis of mixtures of propane with propene causes a higher running concentration of CH_3 radicals, the addition of which to propene at high temperatures does not occur in practice.[79] On pyrolysis of ethane the concentration of methyl radicals which are formed only at the initiation stage is low and correspondingly the contribution of reaction (1*b*) is not appreciable.

According to this scheme the rate constant for the overall decomposition of propene is described by the equation

$$k_{C_3H_6} = k_2[H] + k_{1a}[H] + k_{1b}[CH_3]. \quad (I)$$

Since $k_2 \gg k_{1a}$ it may be taken that

$$k_{C_3H_6} = k_2[H] + k_{1b}[CH_3]. \quad (II)$$

The first term of equation (II) is the specific rate of formation of ethylene from propene which is calculated from the data on the distribution of radioactivity in ethylene and propene. For the pyrolysis of propane with added 1.77 vol.% C_3H_6 the ratio $k_2[H]/k_{1b}[CH_3]$ is 1.5 at 850 °C.[9] Thus in mixtures with a small propene content its rate of reaction with H atoms is at least 1.5 times greater than with methyl radicals. This ratio is reduced with an increase in the propene concentration (Table 2). The ratio of the concentrations of H atoms and methyl radicals therefore changes with the change in the composition of the initial mixture. The concentration of methyl radicals increases with an increase in propene concentration and the contribution of reaction (1*b*) becomes more noticeable.

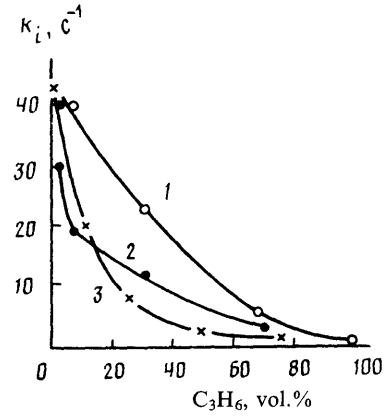


Figure 1. Change in rate constant for (*1*, *3*) the decomposition of propene and (*2*, *3*) the formation of ethylene with the change in composition of the initial mixture at 850 °C; *1*, *2*, mixture of propane and propene;[9] *3*, mixture of ethane and propene.[6]

Table 2. Ratio of hydrogen and methane and also rates of disappearance of propene with the partcipation of H atoms (k_2) and methyl radicals (k_{1b}) on pyrolysis of mixtures of propane and propene (850 °C).

C_3H_6 content in initial mixture, %	$[H_2]/[CH_4]$	$k_2[H]/k_{1b}[CH_3]$
1.77	1.0	1.5
6.41	1.0	1.0
30.78	0.8	1.0
68.18	0.5	0.8

The relative increase in the concentration of CH_3 radicals also shows in the ratio of hydrogen and methane in the pyrolysis products (Table 2).

The efficiency of the inhibitory action of propene is also dependent on reaction (2), since $k_2 \gg k_1$. In addition, in contrast to reaction (1) the conversion of C_3H_6 by reaction (2) leads to replacement of H by the less reactive methyl radical.

The concentration of H atoms is reduced as the concentration of propene in the initial mixture with propane is increased (Fig. 2).[9] In this way the rate of the overall decomposition of propane is also reduced practically in proportion (Fig. 3).

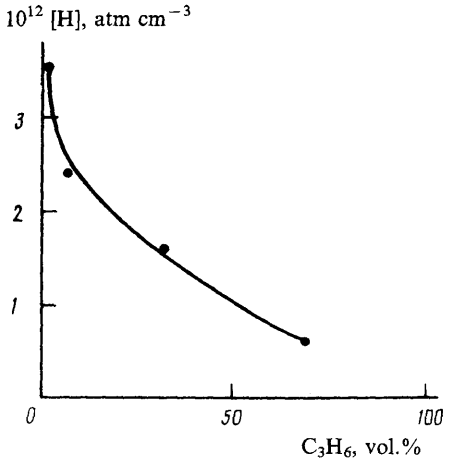


Figure 2. Change in concentration of hydrogen atoms in the pyrolysis zone of mixtures of propane and propene with the change in composition of the initial mixture at 850 °C.

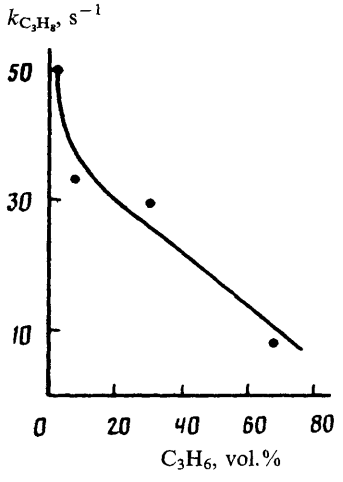


Figure 3. Reduction in the rate constant for propane decomposition with increasing content of propene in the initial mixture at 850 °C.

Propene is also converted according to reactions (1) and (2) on pyrolysis when mixed with n-butane. In this case too the inhibitory action of propene was dependent mainly on reaction (2). As a result the concentration of radicals propagating the chain was reduced and consequently chain propagation involving n-butane itself proceeds at a lower rate.

The inhibitory action of propene on the decomposition of alkanes was reduced on going from ethane to propane and n-butane (Fig. 4).

This is linked with the increase in the contribution of the reactions of methyl radicals which are formed on pyrolysis of propane and n-butane both at the initiation and at the chain propagation stage.

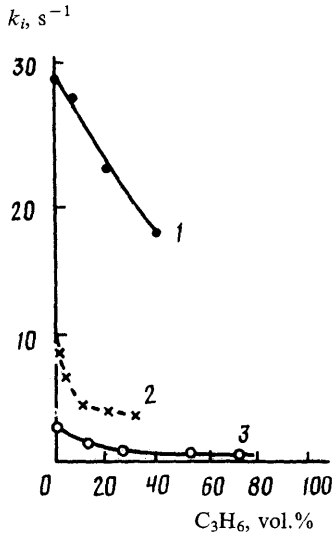


Figure 4. Dependence of the rate constant (k_i) for the decomposition of alkanes on C_3H_6 concentration in the mixture: *1*, $k_{n\text{-}C_4H_{10}}$; *2*, $k_{C_3H_8}$; *3*, $k_{C_2H_6}$, temperature 800 °C.

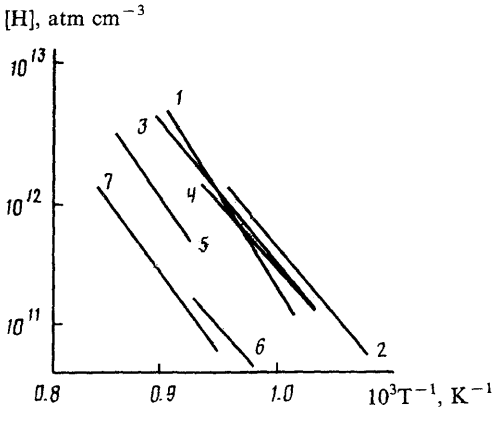


Figure 5. Temperature dependence of the hydrogen atom concentration in the pyrolysis zone of *1*, ethane; *2*, n-hexane; *3*, propane; *4*, n-butane; *5*, 1,3-butadiene, *6*, 1,3-pentadiene and *7*, propene at an overall pressure of 100 mmHg.

On pyrolysis of ethane, propene and butane the concentration of hydrogen atoms is approximately the same (Fig. 5).[80] It is possible to estimate the concentration of methyl radicals from the rate of accumulation of methane. Thus on pyrolysis of ethane the rate of hydrogen formation is more than an order of magnitude greater than the rate of methane formation.[31] On pyrolysis of propane these rates are approximately the same,[9] and on pyrolysis of n-butane methane is formed approximately 1.5 times more rapidly than

hydrogen.[11] Consequently in the pyrolysis of propane and n-butane the contribution of chain propagation reactions involving methyl radicals becomes more marked.

In addition it must be noted that according to the proposed mechanism the extent of the inhibitory action of an additive is determined by the ratio of the reaction rates of H atoms with the alkane and with the inhibitor. The rate constant for the reaction of H atoms with alkanes investigated increases on going from ethane to n-butane.[81] This leads to an increase in the contribution of reactions involving alkane in the series $C_2H_6 < C_3H_8 < n\text{-}C_4H_{10}$ and consequently to a reduction in the inhibitory action of propene on this series of alkanes.

The stronger inhibitory action of propane compared with ethane in the decomposition of propene is explained by the higher overall concentration of the radicals propagating the chains (see Fig. 1). Regrettably due to the lack of data on the pyrolysis of mixtures of n-butane with radioactive propene it is as yet impossible to judge the extent of the inhibitory action of the former on the breakdown of the latter.

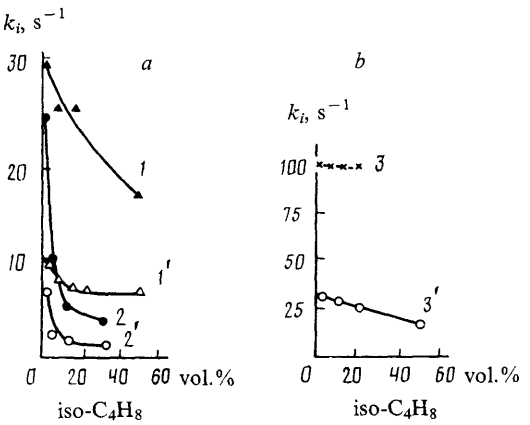


Figure 6. Dependence of the overall rate constant (k_i) for alkane decomposition on the 2-methylpropene concentration in the initial mixture with *a*: *1*, *1'*, propane; *2*, *2'*, ethane and *b*: *3*, 3', n-butane at 850 and 800 °C respectively.

On pyrolysis of mixtures of ethane, propane and n-butane with 2-methylpropene the mutual effect of hydrocarbons on their decomposition is also linked with the competing reactions:

$$R(\dot{H}, \dot{C}H_3) + \text{alkane} \rightarrow RH + R^1,$$

$$H + \text{iso-}C_4H_8 \rightarrow \text{iso-}\dot{C}_4H_9 \rightarrow \dot{C}H_3 + C_3H_6,$$

$$R(\dot{H}, \dot{C}H_3) + \text{iso-}C_4H_8 \rightarrow \text{iso-}\dot{C}_4H_7 + RH.$$

Like propene, 2-methylpropene shows a stronger inhibitory action on the decomposition of ethane (Fig. 6) but n-butane is the strongest initiator of the decomposition of 2-methylpropene (Fig. 7). However propene is a stronger inhibitor of the decomposition of the C_2-C_4 alkanes than 2-methylpropene (Figs. 4 and 6). This is seemingly caused by the higher value of the rate constant for the addition of H atoms to propene.

In principle Niclause and collaborators[22] arrived at the same mechanism of initiation–inhibition, based on literature data and on the results of their own kinetic investigations on the pyrolysis of ethane, isobutane and 2,2-dimethylbutane in the presence of alkenes (ethylene, propene, 2-methylpropene, *trans*-2-butene and two isopentenes, including 2-methyl-3-butene). However these authors considered that the addition of H atoms to the double bond of the inhibitor is responsible for the distribution of the products and the inhibitory action is caused by the removal of H atoms from the alkene.

$$\text{iso-}C_4H_{10} \rightarrow \text{radical formation},$$

$$R(\dot{H}, \dot{C}H_3) + \text{iso-}C_4H_{10} \rightarrow RH + \text{iso-}\dot{C}_4H_9, \qquad (6a)$$

$$R(\dot{H}, \dot{C}H_3) + \text{iso-}C_4H_{10} \rightarrow RH + \text{t-}\dot{C}_4H_9, \qquad (6b)$$

$$\text{iso-}\dot{C}_4H_9 \rightarrow \dot{C}H_3 + C_3H_6,$$

$$\text{t-}\dot{C}_4H_9 \rightarrow \dot{H} + \text{iso-}C_4H_8,$$

$$\dot{H} + C_3H_6 \leftrightarrows \text{sec-}\dot{C}_3H_7,$$

$$\text{sec-}\dot{C}_3H_7 + \text{iso-}C_4H_{10} \rightarrow C_3H_8 + \text{iso-}\dot{C}_4H_9,$$

$$\text{sec-}\dot{C}_3H_7 + \text{iso-}C_4H_{10} \rightarrow C_3H_8 + \text{t-}\dot{C}_4H_9,$$

$$\dot{H} + C_3H_6 \rightarrow \text{pr-}C_3H_7,$$

$$\text{pr-}\dot{C}_3H_7 \rightarrow \dot{C}H_3 + C_2H_4,$$

$$\text{t-}\dot{C}_4H_9 + \text{iso-}C_4H_{10} \rightleftarrows \text{iso-}\dot{C}_4H_9 + \text{iso-}C_4H_{10},$$

$$\dot{H} + C_3H_6 \rightarrow H_2 + \dot{C}_3H_5. \qquad (1a)$$

Chain termination occurs by recombination of CH_3, C_3H_5 and sec-C_3H_7 radicals.

The contributions of the following empirical reactions in the formation of the main products at 470 °C have been estimated for mixtures of propene and isobutane (at $[C_3H_6]/[\text{iso-}C_4H_{10}] = 0.10$).

$$\text{iso-}C_4H_{10} = CH_4 + C_3H_6, \qquad 25.4\%$$

$$\text{iso-}C_4H_{10} = H_2 + \text{iso-}C_4H_8, \qquad 51.2\%$$

$$\text{iso-}C_4H_{10} + C_3H_6 = C_3H_8 + \text{iso-}C_4H_8, \qquad 13.7\% \qquad (7)$$

$$\text{iso-}C_4H_{10} + C_3H_6 = CH_4 + C_2H_4 + \text{iso-}C_4H_8, \qquad 9.2\%$$

This mechanism differs from that given above in that the main route for the conversion of alkyl radicals formed by the addition of H atoms to the double bond of the inhibitor is the removal of a H atom from a molecule of the initial alkane. As a result the inhibitor is converted into the corresponding alkane [empirical reaction (7)]. However using radioactive additives it was shown convincingly that in mixtures with alkanes propene did not give rise to propane in practice. Such a difference is seemingly caused by the different pyrolysis temperatures 450–550 and 750–900 °C respectively.

The mechanism of the high temperature pyrolysis differs from that at lower temperatures by the fact that in practice only methyl radicals and H atoms participate in the chain propagation reactions. Other alkyl radicals are mainly decomposed. At temperatures below 600 °C for C_2-C_4 alkyl radicals not only is decomposition characteristic but also removal of H atoms from the initial alkene occurs.

b. Specific features of the inhibitory action of higher alkenes in the thermal decomposition of alkanes

In the thermal decomposition of mixtures of the higher n-alkanes with alkenes in contrast to mixtures of C_2-C_4 alkanes with propene the alkene is thermally less stable, due to the presence in the molecule of a weak C–C bond in the β-position to the double bond. It was established by low temperature IR spectroscopy in a nitrogen matrix[82,83] that the initiation stage of the decomposition of C_5-C_7 1-alkenes occurs by a radical mechanism under pyrolysis conditions with the formation of an allyl and the corresponding alkyl radical which initiates a radical chain process. It is assumed that in the pyrolysis of mixtures the alkene must initiate the decomposition of the alkane.[84] At the same time it was shown[23,27,28] that the alkene has an inhibitory action on alkane decomposition and the alkane initiates breakdown of the alkene. However the mutual effect is weakly expressed. This is linked with the fact that the alkene on the one hand acts as an initiator of the radical chain decomposition of the n-alkane and on the other as an inhibitor of the chain propagation stage since on pyrolysis the concentration of radicals propagating the chain is lower. Thus at 700–800 °C the concentration of hydrogen atoms in the decomposition of n-hexane is double that in the case of 1-hexene at a comparable concentration of methyl radicals.[85] On pyrolysis of mixtures of n-hexane and 1-hexene the ratio $[H_2]/[CH_4]$ is reduced on increasing the 1-hexene concentration (Fig. 8),[28] which indicates the fall in the relative concentration of H atoms in the reaction mixture. It follows from this that the initiating action of the alkanes is caused mainly by the increased rate of addition of H atoms, generated on decomposition of the n-alkane, to the alkene double bond and also by an increase in the rate of removal of H atoms, shown for the case of 1-hexene:

$$\dot{H} + C{=}C{-}C{-}C{-}C{-}C \longrightarrow \begin{cases} \dot{C}{-}C{-}C{-}C{-}C{-}C, \\ C{-}\dot{C}{-}C{-}C{-}C{-}C, \\ H_2 + C{=}C{-}\dot{C}{-}C{-}C{-}C, \\ H_2 + C{=}C{-}C{-}\dot{C}{-}C{-}C, \\ H_2 + C{=}C{-}C{-}C{-}\dot{C}{-}C, \\ H_2 + C{=}C{-}C{-}C{-}C{-}\dot{C}. \end{cases}$$

As a result the rate of chain propagation for the corresponding alkane is reduced [reaction (8)]

$$H + C{-}C{-}C{-}C{-}C{-}C \longrightarrow \begin{cases} H_2 + \dot{C}{-}C{-}C{-}C{-}C{-}C, & (8a) \\ H_2 + C{-}\dot{C}{-}C{-}C{-}C{-}C, & (8b) \\ H_2 + C{-}C{-}\dot{C}{-}C{-}C{-}C. & (8c) \end{cases}$$

As is known, the rate constant for the chain initiation reaction involving the alkene ($k_{C_nH_{2n}}$) is greater than that for the alkane ($k_{C_nH_{2n+2}}$). However the difference between them is not significant. Consequently the initiation rate of radicals on pyrolysis is determined mainly by the concentration of hydrocarbons in the initial mixture. For mixtures with a high alkene content, knowing that $k_{C_nH_{2n}}[C_nH_{2n}] \gg k_{C_nH_{2n+2}}[C_nH_{2n+2}]$, the alkene is responsible for the initiation of radicals and the decomposition of the n-alkane may be expected to be hastened. But this does not occur due to the low n-alkane concentration and the higher values of the rate constant for chain propagation involving 1-alkene. At the same time the overall concentration of radicals propagating the chain, for which the n-alkane is responsible, is not increased on pyrolysis of such mixtures. Consequently the initiating action of the n-alkane is not apparent in the decomposition of the 1-alkene.

On pyrolysis of mixtures with a low 1-alkene content when the rate of radical formation involving the alkane is at least comparable with the rate of their formation from the 1-alkene, initiation of 1-alkene decomposition by the n-alkane takes place and this effect is more apparent at lower 1-alkene concentrations. For these mixtures a higher concentration of H atoms propagating the chain is more characteristic than for 1-alkene.

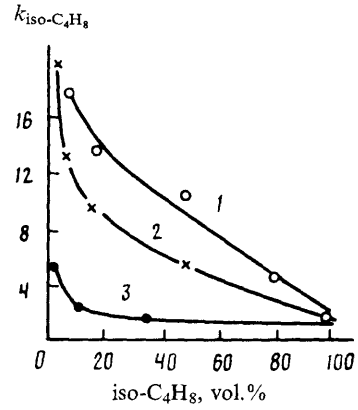


Figure 7. Rate constant for the decomposition of iso-C_4H_8 in mixtures with *1*, n-butane; *2*, propane; *3*, ethane at 800 °C.

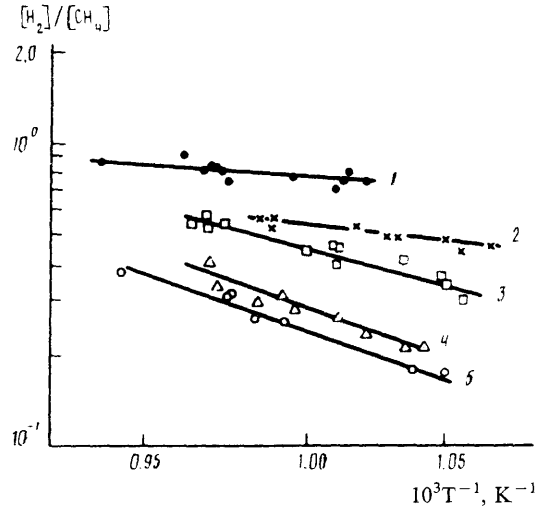


Figure 8. Temperature dependence of the ratio H_2/CH_4 in the pyrolysis products of *1*, hexane; *5*, 1-hexene and mixtures of hexane with *2*, 10% 1-hexene; *3*, 25% 1-hexene and *4*, 75% 1-hexene.

Consequently for the pyrolysis of mixtures of higher alkanes with 1-alkenes the mechanism of the mutual effect is also determined mainly by the competing chain propagation reaction involving

hydrogen atoms. But in contrast to mixtures with propene it is necessary to consider in the decomposition scheme the step of forming radicals involving the 1-alkene. Consequently the rate constants for radical formation in the decomposition of a n-alkane and 1-alkene, and also the concentration of H atoms are not appreciably different, the mutual effect of these hydrocarbons on the rate and route of the decomposition in mixtures is less clearly apparent and depends to a large extent on the composition of the mixture and the pyrolysis temperature.

c) Inhibition–initiation on pyrolysis of binary mixtures of hydrocarbons of other classes

The mutual effect on the rate and route of the decomposition of hydrocarbons on joint pyrolysis is readily explained by the difference in the concentration of the radicals propagating the chain as is the apparent inconsistency of the experimental data observed in the case of a weakly expressed inhibition–initiation effect.[86]

It was shown[80] that there is no significant difference in the concentration of hydrogen atoms formed in the pyrolysis of C_5-C_{15} n-alkanes. In fact at relatively low temperatures a small increase is recorded in the concentration of H atoms with chain length for C_3-C_6 alkanes (see Fig. 5). At the same time a very high concentration of hydrogen atoms exists in the pyrolysis at temperatures above 800 °C. Consequently at relatively low temperatures the n-alkanes show an initiating action on ethane decomposition which disappears at high temperatures.[49] The initiating action of ethane on the decomposition of n-alkanes at high temperatures may be apparent only in mixtures with a high ethane concentration, since only in this case can a higher concentration of H atoms be brought about in a mixture than on pyrolysis of an individual n-alkane. Thus a change in the composition of the initial alkane mixture and of the pyrolysis temperature leads to an inversion of the mutual effect.

Table 3. Concentration of radicals (mol litre^{-1}) on pyrolysis of hydrocarbons and their equimolar mixtures (660 °C).[37]

Starting material	$10^{11}[H]$	$10^{9}[CH_3]$	$10^{10}[C_2H_5]$
Propane	2.4	3.2	1.1
Isobutane	3.4	5.1	–
Neopentane	1.4	6.3	1.9
Propane + Neopentane	7.3	8.4	1.1
Isobutane + Neopentane	4.6	9.1	–

The thermal stability of the components of a mixture does not play a significant role. This is indicated by data on the pyrolysis of five binary equimolar mixtures based on ethane, propane, n- and isobutane and pentane at 650–690 °C.[37] It transpires that neopentane accelerates the decomposition of both the thermally less stable isobutane and of the thermally more stable propane. The decomposition rate of neopentane itself in the mixtures was practically unchanged. The authors of this study also arrived at the conclusion that the initiating action of a hydrocarbon on pyrolysis in a mixture is linked with the change in the concentration of the radicals propagating the chain at the expense of the partner (see Table 3).

As is seen from Table 3 $[R]_{C_3H_8} < [R]_{neo\text{-}C_5C_{12}}$ and $[R]_{iso\text{-}C_4H_{10}} < [R]_{neo\text{-}C_5H_{12}}$. However the concentration of the radicals driving the chain is greater in the case of the pyrolysis of mixtures of these hydrocarbons with neopentane. Consequently in the pyrolysis of mixtures chain propagation reactions proceed at a high rate due to the radicals generated on decomposition of neopentane. Since $[R]_{iso\text{-}C_4H_{10}} > [R]_{C_3H_8}$ and $[R]_{mix}/[R]_{iso\text{-}C_4H_{10}} < [R]_{mix}/[R]_{C_3H_8}$, the initiating actionof neopentane in the decomposition of propane is stronger than in the decomposition of isobutane.

Ethane, like propene, inhibits isobutane pyrolysis, but to a lesser exent.[48] In both cases the mechanism of the inhibition is described by competing reactions of chain propagation with the participation, mainly, of hydrogen atoms. In the case of mixtures of isobutane with C_2H_6 the reactions are:

$$\dot{H} + \text{iso-}C_4H_{10} \rightarrow H_2 + \text{iso-}\dot{C}_4H_9, \qquad (6a)$$

$$\dot{H} + \text{iso-}C_4H_{10} \rightarrow H_2 + \text{t-}\dot{C}_4H_9, \qquad (6b)$$

$$\dot{H} + C_2H_6 \rightarrow H_2 + \dot{C}_2H_5, \qquad (5)$$

and in the case of isobutane with propene they are reactions (2) and (6*a*, *b*). The extent of the inhibitory action is determined by the ratio of the concentration of hydrogen atoms formed in the decomposition of ethane and propene. Since $[H]_{C_3H_6} \ll [H]_{iso\text{-}C_4H_{10}} > [H]_{C_2H_6}$, the rate of reaction (6) in the pyrolysis of mixtures is less than in the decomposition of pure isobutane.

The weaker inhibitory action of ethane compared with propene is linked with the fact that $[H]_{C_2H_6} \gg [H]_{C_3H_6}$ and consequently $[H]_{mix}/[H]_{C_2H_6} \ll [H]_{mix}/[H]_{C_3H_6}$.

In mixtures with other partners such as cyclohexane‡ ethane, like 1-hexene, displays an initiating action[57,87] which is caused by different ratios of the concentrations of H atoms, i.e. $[H]_{C_2H_6} \gg [H]_{cyclo\text{-}C_6H_{12}} < [H]_{C_6H_{12}}$.[80,85]

1,3-Butadiene acts both as an inhibitor and as an initiator of decomposition depending on the partner. On pyrolysis 1,3-butadiene shows an initiating action when mixed with propene.[88] At the same time 1,3-butadiene inhibits the decomposition of ethane.[31] The mechanism of inhibition–initiation on pyrolysis of these mixtures is determined in the first case by the competing reactions (2) and (9):

$$H + C_4H_6 \longrightarrow \dot{C}_4H_7 \longrightarrow \dot{C}_2H_3 + C_2H_4, \qquad (9)$$

and in the second by reactions (5) and (9). But in the first case $[H]_{C_3H_6} < [H]_{C_4H_6}$, and in the second $[H]_{C_2H_6} > [H]_{C_4H_6}$. Consequently in mixtures with propene, reaction (9) proceeds more slowly and in mixtures with ethane more rapidly than in pyrolysis of 1,3-butadiene alone.

The mechanism of the initiating action of allene on the thermal decomposition of hydrocarbons of various classes is described[34–36] by the bimolecular reaction (10)

$$C_3H_4 + RH \longrightarrow \dot{C}_3H_5 + R, \qquad (10)$$

‡ The radical chain character of cyclohexane pyrolysis with the formation of allyl and methyl radicals at the initiation stage was confirmed[83,88] by low temperature IR spectroscopy in a nitrogen matrix and also with radioactive additives.

providing the initiation stage is not unambiguous. The use of only small additions of allene (0.2–1.5%) and the lack of data on the effect of the partner on the rate and course of the decomposition of allene itself does not give a complete picture of the mutual effect of these hydrocarbons on pyrolysis in mixtures.

The allyl radical formed by reaction (10) being itself fairly reactive at relatively low temperatures in chain propagation reactions, [90] is mainly decomposed at relatively high temperatures under pyrolysis conditions generating H atom and the initial allene. It may therefore be suggested that allene does not simply initiate the radical formation stage but also acts as an additive which participates in the radical chain decomposition of the partner accompanied by an increase in the concentration of the radicals propagating the chains.

VIII. Conclusion

The vast majority of data considered above on the pyrolysis of mixtures of various classes of hydrocarbons is most adequately interpreted on the basis of ideas on the role of the components of the mixture in generating hydrogen atoms (and methyl radicals) the concentration of which controls the rate of chain propagation. This mechanism not only describes well the principles of the pyrolysis of mixtures of hydrocarbons of various classes but also enables the efficiency and course of action of one hydrocarbon on the decomposition of another to be explained as a function of its chemical structure and the reaction conditions. It also explains the non-additivity of product formation on pyrolysis of mixtures. The particularly significant deviation from additivity observed in the pyrolysis of alkanes with added propene and 2-methylpropene is caused by the rapid addition of hydrogen atoms to the alkene. The concentration of hydrogen atoms is greater than in the pyrolysis of the alkene alone. Under these conditions propene is decomposed mainly to methane and ethylene but the reaction associated with the formation of the hydrocarbons C_3H_4 and C_2H_2 is almost completely suppressed.

A deviation of the yield of products from additivity was observed even in the case of the pyrolysis of mixtures of the higher n-alkanes and 1-alkenes when the mutual effect of the hydrocarbons on the rate of decomposition is insignificant. This is linked with the high rate of reaction of 1-alkenes involving radicals generated in the decomposition of the alkane and mainly the addition of H atoms at the double bond. Since the selectivity of forming products is reduced on increasing the hydrocarbon chain length, it is difficult to separate the key course of decomposition of the 1-alkene and consequently to change significantly the selectivity of forming products in the mixture.

On pyrolysis of mixtures the mutual effect of one hydrocarbon on the thermal decomposition of another is therefore effected by a single mechanism based on competing chain propagation reactions involving the partner hydrocarbons, the rates of which are limited by the concentration of radicals progressing the chain. A single hydrogen may on copyrolysis act in some cases as an initiator and in others as an inhibitor of a process. The main characteristic of a hydrocarbon as an inhibitor is that the concentration of radicals propagating the chain and generated in the pyrolysis process is lower than that of its partner. The inhibition–initiation phenomenon of the radical chain process in the pyrolysis of mixtures is determined by a change in the concentration of radicals progressing the chain compared with that observed on pyrolysis of the individual hydrocarbons. In this way the thermal stability and the ability of a hydrocarbon to generate radicals unreactive in chain propagation reactions (for example radicals of the allyl type) are not determining and are important only as factors influencing the establishment of a definite level of radical concentration.

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