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G. Vanhove, M. Ribaucour, R. Minetti. On the influence of the position of the double bond on the low-temperature chemistry of hexenes. *Proceedings of the Combustion Institute*, 2005, 30 (1), pp.1065-1072. 10.1016/j.proci.2004.08.042 . hal-01738420

HAL Id: hal-01738420

<https://hal.science/hal-01738420>

Submitted on 14 Sep 2020

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**On the influence of the position of the double bond on the low-temperature
chemistry of hexenes**

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Colloquium: Reaction Kinetics

Short title: Low-temperature chemistry of isomeric hexenes

Abstract

The chemistry of oxidation and autoignition of 1-, 2-, and 3-hexene has been studied after rapid compression between 630 and 850 K for stoichiometric mixtures with "air". The phenomenology of autoignition has been recognized and intermediate products formed before autoignition have been identified and analyzed. They comprise mainly hexadienes, O-heterocycles and aldehydes. There are many common products, because some of the intermediate alkenyl or alkenylperoxy radicals are delocalized. Saturated O-heterocycles are specific products formed by addition of HO₂ to the double bond. Unsaturated O-heterocycles are products typical of the long alkenyl chain. Saturated and unsaturated lower aldehydes are the products of OH addition to the double bond of hexenes and hexadienes. The relative abundance of the intermediates enables a better insight into the competition between the reactivity of the double bond and the reactivity of the alkenyl chain. According to the position of the double bond, the behavior of 3-hexene is dominated by the properties of the double bond whereas the behavior of 1-hexene is dominated by the properties of the alkenyl chain. The reactivity of the alkenyl chain is related to the type and number of C-H bonds, the ability of stabilized radicals to react, and the cyclic strain of the transition state of isomerization reactions. Therefore, 1-hexene reacts much more with the typical features of alkanes like a two-stage ignition with a cool flame and a negative temperature coefficient. 3-Hexene does not have typical features and 2-hexene has an intermediate behavior.

243 words

Keywords: autoignition, oxidation, hexenes, low-temperature

Introduction

The oxidation and autoignition of aliphatic saturated hydrocarbons in air at high pressures and in the low- and intermediate-temperature range (600-900 K) has been the object of many experimental and modeling studies [1]. It appears that the kinetics of oxidation in adiabatic conditions presents complex patterns such as a non-Arrhenius behavior and thermokinetic interactions. Much fewer studies have been published on the oxidation of long chain alkenes in the same temperature and pressure conditions [2-7], although alkenes are major intermediate products of alkane oxidation.

In this work, isomers of hexene have been chosen to recognize the influence of the position of the double bond on the low-temperature chemistry of oxidation under high pressure. Autoignition delays and intermediate product concentrations were measured using a rapid compression machine.

1. Experimental

Autoignition delay times of stoichiometric mixtures of 1-hexene, trans-2-hexene, and trans-3-hexene/"air" mixtures have been measured in the rapid compression machine of Lille between 6.8-8.5 bar, and 630-850 K according to a methodology already used for alkanes and aromatics [8,9]. The reaction volume is a cylinder of 38 cm³ and the compression ratio is 9.3. The compressed gas temperature (T_c) was varied by changing the composition of the inert gas (N₂, Ar, CO₂) and calculated according to an adiabatic core gas model [10]. In this study, two series of experiments were conducted. In the first series, the pressure and light emission traces were recorded for 11 different compositions of the inert gas. In the second series, the chemical composition of the reactive mixtures for each of the hexenes were analyzed qualitatively and quantitatively by gas chromatography and mass spectrometry at a selected time before autoignition.

2. Phenomenology of autoignition

Figure 1 presents typical experiments of autoignition by compression of the three hexenes and cyclohexene [11] for sake of comparison. The initial charges were identical and the inert gas had the same composition leading to the same temperature T_c (725 K) and pressure (9.4 bar). The pressure and the light emission traces exhibit a two-stage ignition with an intense cool flame for 1-hexene, a two-stage

ignition with a weak cool flame for 2-hexene, and a one-stage ignition with a very faint light effect for cyclohexene and 3-hexene.

The general characteristics of autoignition were studied by changing T_c . Figure 2 presents the evolution of the delay times versus T_c . The phenomenology of autoignition depends markedly on the position of the double bond. For 1-hexene the evolution is not very different from that of alkanes studied in the same conditions [8]. However, the typical features of thermokinetic interactions are not so well-marked. Autoignition occurs in two stages with a cool flame pre-ignition up to 800 K and a slight negative temperature coefficient (NTC) is visible between 750 and 830 K. For 2-hexene, the typical features are still less marked. There is a two-stage ignition with a weak cool flame, which disappeared above 730 K. No NTC is observed but rather a very slow decrease of the ignition delay time between 720 and 815 K with a distinct inflexion point around 780 K. For 3-hexene and cyclohexene, the phenomenology of autoignition is plainer. There is no cool flame, nor NTC but only a faint inflection point near 730 K for 3-hexene and 740 K for cyclohexene.

Clearly the position of the double bond has an impact on the reaction pathways responsible for the onset of the cool flame, the autoignition delay time, and the dependence of the delay time on T_c .

3. Analysis of intermediates

The analyses were performed during the delay at $T_c = 710$ K. A rapid adiabatic expansion of the gas into a collecting vessel was allowed, so that all reactions were quenched. Samples of 1- and 2-hexenes were taken after the cool flame. The hydrocarbon consumption was about 10 % for 1-hexene and 15 % for 2-hexene. In the case of 3-hexene, the time of sampling was fixed at 90 % of the delay time, corresponding to a consumption of only a few percent of the hydrocarbon. Analyses were made for the three isomers in strictly identical chromatographic conditions. This procedure made the identification of the intermediates much easier and the intermediates common to two or three isomers were easily recognizable. The structures of the intermediates were recognized by analysis of their mass spectrum. All concentrations were obtained using an internal standard and expressed as the number of C atoms per 100 initial C in the fuel [11].

Table 1 gives the selectivities of C_6 intermediates and C_2 - C_5 aldehydes: the selectivity is the ratio of the quantity of the intermediate to the total quantity of analyzed intermediates and is expressed in

percent. Intermediates of Table 1 represent 60, 75, and 95 % of the analyzed intermediates of 1-, 2-, and 3-hexene respectively, the remaining being mainly lighter alkenes and oxygenates. They are sorted out according to the chemical families together with an acronym to facilitate the discussion.

4. Main reaction pathways

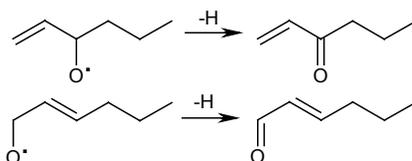
A previous study of auto-ignition of *n*-pentane and 1-pentene in the same range of temperature and pressure has shown that the scheme of oxidation of alkenes is more complex than the scheme of oxidation of alkanes because alkenes are also oxidized by reactions specific to the presence of the double bond: the addition of radicals OH and HO₂ to the double bond [5,6]. Figure 3a shows the main reaction groups which will be discussed in this publication. The groups (i) and (ii) refer to the reactivity of the double bond of the alkene RH towards OH and HO₂. The groups (iii) and (iv) refer to the reactivity of the alkyl chain.

The group (i) is a sequence of propagation reactions leading to the cleavage of the double bond. The addition of OH to the double bond is followed by a peroxidation of the resulting hydroxyalkyl radical °Q'OH, an internal H-transfer between two oxygen atoms, and finally a C-C scission into two aldehydes closing the propagation cycle by returning OH [12,13,14]:

$$\text{RH} + \text{OH} \longrightarrow \text{°Q'OH} \xrightarrow{\text{O}_2} \text{°O}_2\text{Q'OH} \longrightarrow \text{Ald1} + \text{Ald2} + \text{OH}.$$

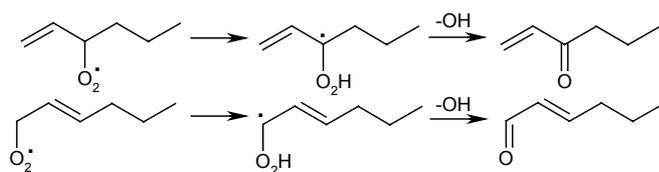
The group (ii) is a sequence transforming HO₂ into OH. The addition of HO₂ to the double bond produces an excited hydroperoxyalkyl radical °Q'O₂H* [15]. The cleavage of the O-O weak bond coupled with a cyclization gives the oxirane: RH + HO₂ → °Q'O₂H* → Q'O + OH. The same type of hydroperoxyalkyl radical is also produced in the oxidation scheme of alkanes but, in that case, it is not in an excited state as it is generated through an internal H-transfer in an alkylperoxy radical. In the case of alkenes, it has been observed that the excited °Q'O₂H* can undergo isomerizations, °Q'O₂H* → RO₂°, to produce alkylperoxy radicals RO₂° of the parent alkane [5,6,16]. As a consequence, some oxidation products of an alkene are identical to those of the parent alkane. They are produced through various bond scissions of hydroperoxyalkyl radicals: O-heterocycles by O-O scission and lower aldehydes by β C-C scission.

The groups (iii) and (iv) are sequences of reactions initiated by an H-abstraction from the alkyl chain of the alkene and producing an alkenyl radical R° . This abstraction and the following reactions are common to the oxidation scheme of alkanes. However, differences in reactivity are expected in the case of alkenes because alkyl as well as allylic C-H bonds can be broken. Allylic bonds are the weakest bonds and their scission leads to a resonance-stabilized radical. Stabilized radicals are long living radicals, which may react by a termination reaction with the weakly reactive radical HO_2 to form a thermally unstable peroxide RO_2H . This peroxide can be considered as a degenerate branching agent, which will decompose into the two radicals RO° and OH . The termination reaction and the following delayed branching reaction are often taken for granted in the case of the highly stabilized benzyl radical [17,18]. Unsaturated aldehydes and ketones can be formed from RO° after the abstraction of the allylic H linked to the C atom with the oxy function:



The group (iii) involves an allylic H-abstraction by O_2 leading to an alkadiene DiN, either directly through $R^\circ + O_2 \rightarrow DiN + HO_2$, or indirectly through the sequence $R^\circ + O_2 \rightarrow RO_2 \rightarrow {}^\circ QO_2H \rightarrow DiN + HO_2$. As shown by theoretical studies on the system ethyl + O_2 , the direct and indirect pathways are not incompatible [19,20]. Alkadienes can also undergo reactions of group (i) to give saturated and unsaturated aldehydes.

The group (iv) involves the peroxidation of R° , its isomerization into a hydroperoxyalkenyl radical ${}^\circ QO_2H$, and various bond scission of ${}^\circ QO_2H$. The products of this sequence are O-heterocycles QO , formed by a O-O scission and cyclization, and lower aldehydes formed by a β C-C scission (not presented in Figure 3a), with the peculiarity that they have a double bond. The isomerizations of RO_2° involving an allylic H-transfer will be favored. The peroxidation of allylic R° is not favored because of the relatively shallow well of $75\text{-}90\text{ kJ}\cdot\text{mol}^{-1}$ compared to $134\text{-}155\text{ kJ}\cdot\text{mol}^{-1}$ for alkyl radical [21,22]. However, it can be followed by an internal transfer of the allylic hydrogen of RO_2° producing an allylic radical ${}^\circ QO_2H$ and restoring the resonance delocalization. Then, the O-O scission of ${}^\circ QO_2H$ will produce an alkenone or an alkenal as in the following reactions:

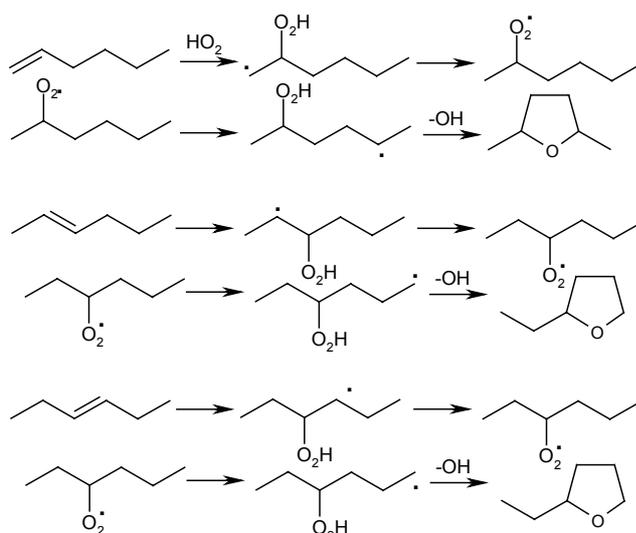


A similar internal transfer of benzylic hydrogen was also proposed to explain the formation of aldehydes in the case of benzylperoxy radicals [9].

5. Application to hexenes

The qualitative and quantitative analysis of the oxidation products has allowed to recognize the dominant pathways of oxidation of 1-hexene (Figure 3b), 2-hexene (Figure 3c), and 3-hexene (Figure 3d) among the many pathways described above. The formation of products will be discussed following the order of Table 1.

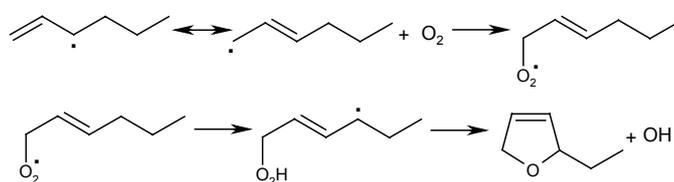
$C_6H_{12}O$ products are formed by reactions of group (ii). The oxiranes are formed readily: HexN1 gives ButOxi, HexN2 gives MeProOxi, and HexN3 gives Et2Oxi. The reactions leading to oxiranes are correlated to the alkene ionization energy [24]. HexN2 and HexN3, which have a lower ionization energy (8.85 ± 3 eV) than HexN1 (9.37 eV) [25], have a higher yield in oxirane. The other $C_6H_{12}O$ O-heterocycles may result from a isomerization of the adduct $^{\circ}Q'O_2H^*$: HexN1 gives diMeTHF, HexN2 gives EtTHF, and HexN3 gives EtTHF as shown below:



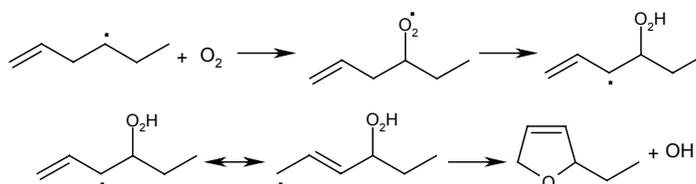
The strain in the cyclic transition states of isomerization and cyclization limits the formation of other O-heterocycles. The saturated aldehydes and ketones are more difficult to justify by a isomerization

sequence because the internal transfer through a four-centers transition state is unfavorable [23]. However, as ${}^{\circ}\text{Q}'\text{O}_2\text{H}^*$ is in an excited state, one can surmise that they would be possible.

$\text{C}_6\text{H}_{10}\text{O}$ products are formed by reactions of group (iv). They include unsaturated O-heterocycles and unsaturated aldehydes or ketones. To understand the formation of some of them, it must be noticed that the same radical R_1° delocalized on carbon atoms 1 to 3 will be formed by HexN1 and HexN2, whereas another common radical R_2° delocalized on carbon atoms 2 to 4 will be formed by HexN2 and HexN3. The two products MeVinOxet and VinTHF are common to HexN1 and HexN2 and are the result of the delocalization of R_1° . This delocalization could justify the production of EtDHF from HexN1 by the following sequence:



If this sequence occurs, EtDHF would also be produced by HexN2 as R_1° is also formed by HexN2, but it is not the case. The following sequence involving a delocalized radical ${}^{\circ}\text{QO}_2\text{H}$ is more probable because addition of O_2 to an alkyl radical is faster than in the case of an allylic radical:



The reactions producing unsaturated aldehydes and ketones indicate internal transfers of an allylic H through a four-centers transition state: HexN1 \rightarrow HexN2Al and HexN1On3; HexN2 \rightarrow HexN1On3, HexN3On2, and HexN2Al; HexN3 \rightarrow HexN3On2 and HexN4On3. As already mentioned, unsaturated C_6 aldehydes and ketones might also be formed by termination reactions between allylic alkenyl radical and HO_2 .

Most of the hexadienes C_6H_{10} are formed by reactions of group (iii) after the initial abstraction of an allylic hydrogen: HexN1 gives DiN13, HexN2 and HexN3 give both DiN13 and DiN24. The other hexadienes are formed from the alkyl chain of HexN1 by an initial non-allylic abstraction: HexN1 gives DiN14 and DiN15. The formation of DiN24 from HexN1 is unexpected.

The C₂-C₅ saturated aldehydes are formed mainly by reactions of group (i). HexN1 gives PenAl and MeAl, HexN2 gives EtAl and BuAl, HexN3 gives only ProAl. There are probably other routes leading to EtAl and MeAl by successive degradations of the hydrocarbon chain or by the addition of OH to hexadienes. Most of ProAl produced by HexN1 and HexN2 would result from addition of OH to DiN13 and the relatively high yield of unsaturated C₃-C₅ aldehydes may result from an addition of OH to the early formed hexadienes.

6. Comparative pathways

Figure 4 shows the comparison between the distribution of families of products reported in Table 1. Only the C₆ unsaturated O-heterocycle family shows a clear decrease in selectivity from HexN1 to HexN3. Their selectivities decrease as the light intensities of the cool flames of Figure 1 from HexN1 to HexN3 (Table 2). In the case of long chain alkenes, the unsaturated O-heterocycles can be considered as typical products of cool flame chemistry as are the saturated O-heterocycles in the case of alkanes.

Propagation reactions (ii) which form oxiranes and other C₆H₁₂O products transform the poorly active HO₂ into the very active OH, whereas propagation reactions (iii) which form hexadienes transform OH into HO₂ (Figure 3b,c,d). The ratio of selectivities C₆H₁₂O/C₆H₁₀ decreases from HexN1 to HexN3 as the autoignition delay time increases (Table 2). The high yield in hexadienes for HexN3 may give rise to an intense production of the degenerate branching agent H₂O₂ by recombination of HO₂. However, branching to the final autoignition will occur only when the temperature is high enough, an event that will occur very late for HexN3 because no cool flame brings about a rise in temperature.

7. Phenomenology clarified

Cool flames are believed to be the result of the decomposition of low-temperature branching agents (LTBA). In the case of alkenes, these agents can be formed by sequences (a) and (b):

– (a) $R^\circ \xrightarrow{O_2} RO_2^\circ \longrightarrow {}^\circ QO_2H \xrightarrow{O_2} {}^\circ O_2QO_2H \longrightarrow \text{LTBAa}$ where R[°] is an alkenyl radical.

– (b) $RH + HO_2 \longrightarrow {}^\circ Q'O_2H^* \xrightarrow{O_2} {}^\circ O_2Q'O_2H \longrightarrow \text{LTBAb}$ where RH is an alkene.

Simulation works [6,26] have shown that the competition between these sequences plays a determining part in the onset of autoignition. Branching agents are unstable species that escape usual analytical

methods. However, their formation is competitive to reactions producing detectable intermediates, produced by the decomposition of $^{\circ}\text{QO}_2\text{H}$ in sequence (a) and by the decomposition of $^{\circ}\text{Q}'\text{O}_2\text{H}^*$ in sequence (b). The yield in these intermediates can help to deduce the relative importance of sequences (a) and (b) in producing the cool flames. The sequence (a) is competitive to the formation of unsaturated O-heterocycles by reaction (iv), whereas the sequence (b) is competitive to the formation of the oxirane Q'O by reaction (ii). HexN1 produces more unsaturated O-heterocycles, an intense cool flame, and less oxirane Q'O than HexN2 and HexN3. HexN3 produces neither unsaturated O-heterocycle, nor cool flame but a higher amount of the oxirane Q'O. One can conclude that sequence (b) does not contribute to the cool flame occurrence.

A decreasing intensity of the NTC is observed from HexN1 to HexN3 (Figure 2). The NTC of alkanes is due to exothermic reversible additions of O_2 to alkyl and hydroperoxyalkyl radicals. If one considers that the alkyl-type radicals undergoing a fast equilibrium with O_2 are formed mainly by H-abstraction from non-allylic CH_2 groups, then such fast equilibria must be more probable for HexN1 with four non allylic secondary H than for HexN2 with only two, and HexN3 with none.

Conclusion

The position of the double bond inside the hydrocarbon chain of C_6 alkenes has a strong impact on the low- and intermediate-temperature chemistry of oxidation leading to autoignition, knock, and pollutant formation. The double bond undergoes reactions with radicals HO_2 and OH leading either to an epoxidation or to a scission of the double bond. The alkyl chain undergoes reactions typical of alkanes. The behavior of long chain alkenes is the result of a competition between these two processes. The reactivity of the double bond is partly dependent of its ionization potential whereas the reactivity of the alkenyl chain depends on the type of C-H bonds, on the ability of the allylic carbon to add oxygen and HO_2 , and on the length of the chain. When the alkenyl chains are short as in 3-hexene or rigid as in cyclohexene, the phenomenology of autoignition is plain and dominated by the reactivity of the double bond. When the alkenyl chain is long, autoignition occurs in two stages as in alkanes. This knowledge should help to model and predict the particularly complex behavior of long chain alkenes.

Acknowledgments

This work was supported by the "Action de Recherche Coordonnée CNRS/Total/Peugeot Citroën".

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Table 1

Percent selectivities of the main intermediates characteristic of the low-temperature chemistry of oxidation (tr. is for traces)

	<i>Symbol</i>	<i>1-hexene</i>	<i>2-hexene</i>	<i>3-hexene</i>
<i>C₆ saturated O-heterocycles C₆H₁₂O</i>				
butyloxirane	ButOxi	2.39	-	-
2-methyl-3-propyloxirane	MeProOxi	-	4.26	-
1,2-diethyloxirane	diEtOxi	-	-	6.11
2,4-dimethyltetrahydrofuran	diMeTHF	1.85	-	-
2-ethyltetrahydrofuran	EtTHF	-	0.53	0.99
<i>C₆ saturated aldehydes and ketones C₆H₁₂O</i>				
hexanal	HexAl	0.98	-	-
2-hexanone	HexOn2	0.76	0.53	-
3-hexanone	HexOn3	-	0.09	0.59
<i>C₆ unsaturated O-heterocycles C₆H₁₀O</i>				
2-methyl-4-vinylloxetane	MeVinOxet	2.39	0.71	-
2-vinyltetrahydrofuran	VinTHF	2.28	tr.	-
2-ethyl-2,5-dihydrofuran	EtDHF	1.19	-	-
<i>C₆ unsaturated aldehydes and ketones C₆H₁₀O</i>				
2-hexenal	HexN2Al	0.76	0.09	-
1-hexen-3-one	HexN1On3	tr.	0.18	-
3-hexen-2-one	HexN3On2	-	0.27	0.20
4-hexen-2-one	HexN4On2	-	0.89	3.75
4-hexen-3-one	HexN4On3	-	-	0.20
<i>hexadienes C₆H₁₀</i>				
1,3-hexadiene	DiN13	2.93	4.88	9.66
1,4-hexadiene	DiN14	0.43	-	-
1,5-hexadiene	DiN15	0.65	-	-
2,4-hexadiene	DiN24	0.87	4.61	11.83
<i>C₂-C₅ saturated aldehydes</i>				
ethanal	EtAl	13.03	23.14	9.07
propanal	ProAl	8.90	6.12	34.52
butanal	ButAl	-	13.74	0.39
pentanal	PenAl	10.53	-	-
<i>C₃-C₅ unsaturated aldehydes</i>				
propenal	ProNAI	9.66	9.40	5.33
2-butenal	ButNAI	0.11	4.88	5.52
pentenal	PenNAI	2.28	3.01	0.99

Table 2

Reactivity characteristics of the isomers of hexene in the condition of analysis

reactivity characteristics	HexN1	HexN2	HexN3
selectivity of unsaturated O-heterocycles	5.9	0.71	0
light intensity of the cool flame	intense	weak	none
ratio of selectivities $C_6H_{12}O/C_6H_{10}$	1.23	0.85	0.36
autoignition delay time / ms	25	46	88

Figure captions

Figure 1. Pressure (thick line) and light emission (thin line and arbitrary unit) traces after a rapid compression to 725 K and 9.4 bar for 1-hexene (a), 2-hexene (b), cyclohexene (c), and 3-hexene (d).

Figure 2. Cool flame (black symbols) and total (white symbols) delay times vs. core gas temperature for 1-hexene (circle), 2-hexene (triangle), cyclohexene (diamond), and 3-hexene (square).

Figure 3. Main low-temperature groups of reactions in the oxidation of alkenes (a). Application to 1-hexene (b), 2-hexene (c), and 3-hexene (d).

Figure 4. Comparative distribution of families of products of 1-hexene (dark gray), 2-hexene (light gray), and 3-hexene (black).

Figure 1

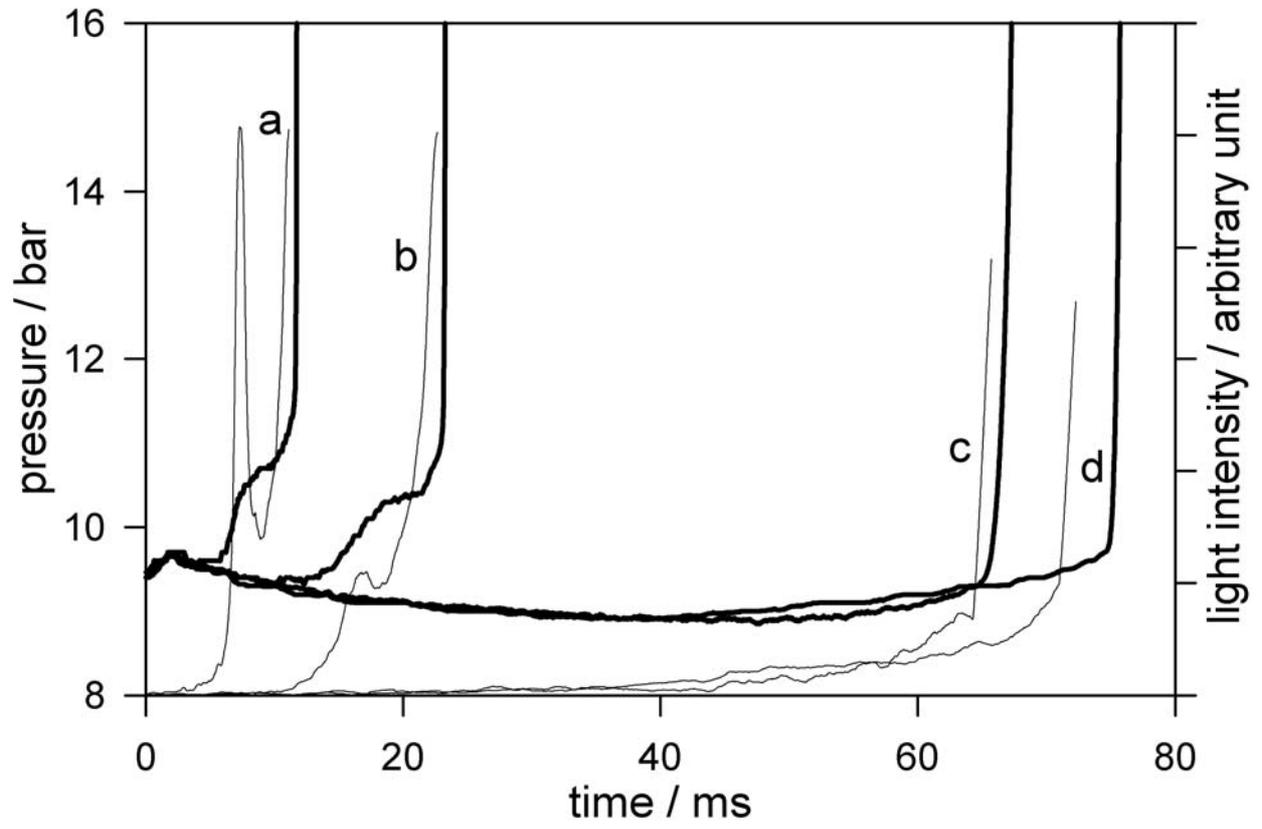


Figure 2

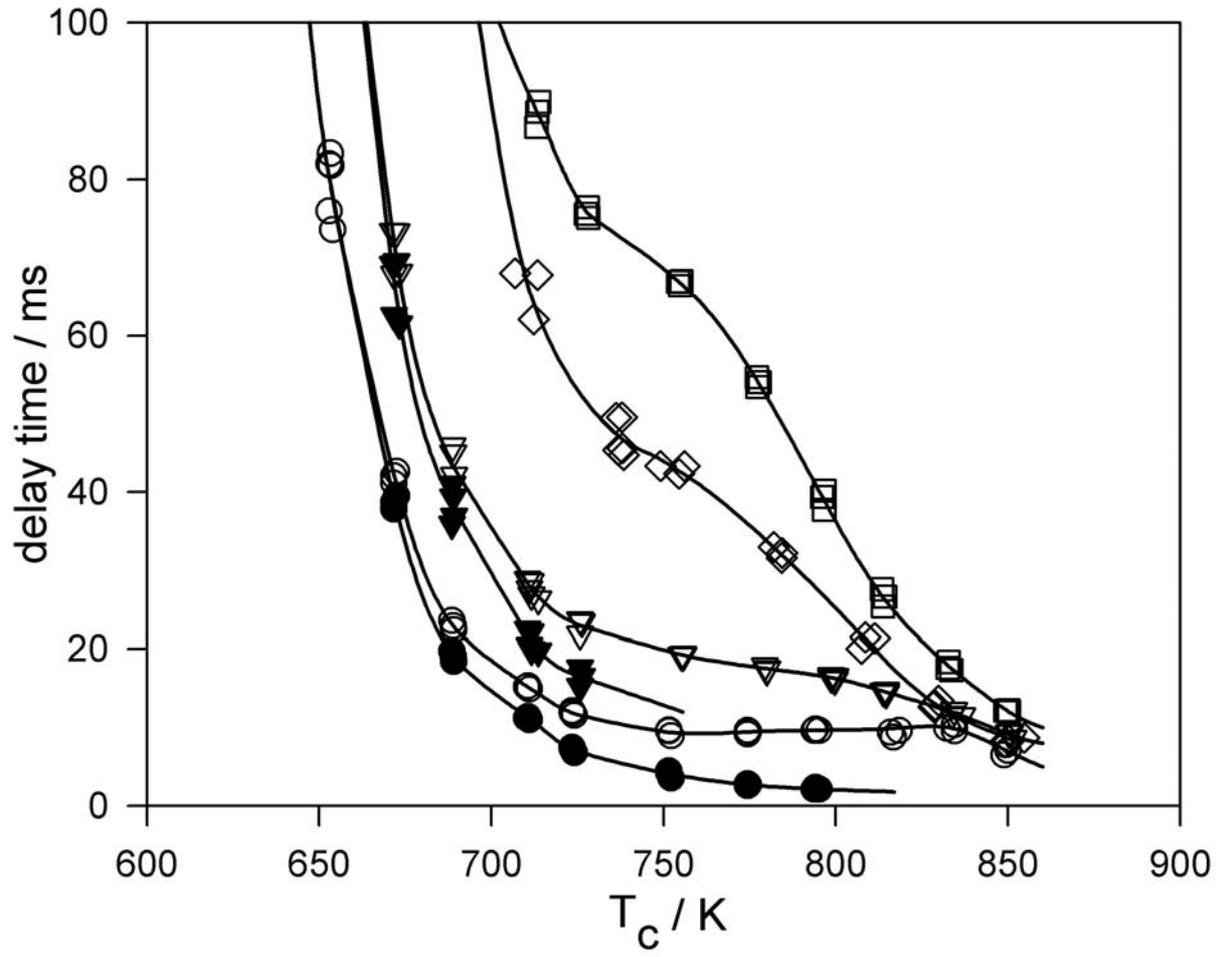


Figure 3

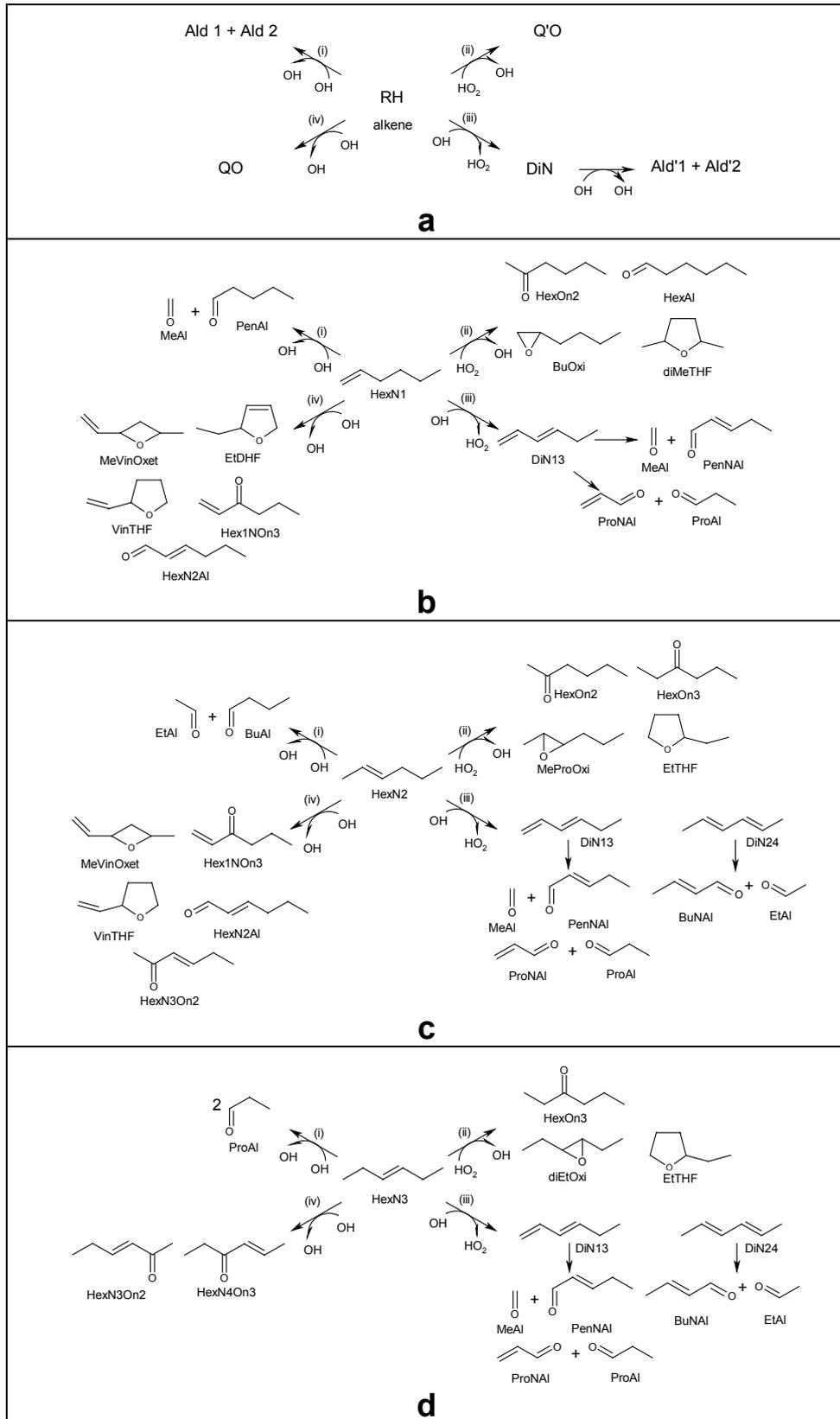


Figure 4

