1362. *Kinetics and Mechanism of the Thermal Decomposition of 4-Methylpent-1-ene*

By M. Taniewski

The thermal decomposition of 4-methylpent-1-ene, investigated in the range 25—200 mm. at four temperatures between 470 and 530°, is strictly first-order under the experimental conditions. The rate constants are fitted by the Arrhenius equation $k = 5{\cdot}0 \times 10^9 \exp(-44200/RT)$ sec.$^{-1}$. Gas chromatography indicated that propene was the major primary product. In the presence of different amounts of nitric oxide up to about 400 mm., the initial rates were not much affected by nitric oxide, unlike the rates of pressure change at very high conversions. The presence of nitric oxide considerably affects the composition of the products even at the initial stages of the decomposition, causing a sharp decrease in the yields of all except propene. A free-radical chain mechanism has been postulated based on the allyl radical as principal chain-carrier. This accounts satisfactorily for the observed kinetics and analytical results, the activation energy for the abstraction of hydrogen from 4-methylpent-1-ene by the allyl radical is estimated to be about 12 kcal. mole^{-1}.

The complexity of the reactions occurring during the thermal decomposition of olefins, and of higher members of the series in particular, leaves the mechanism of the decomposition obscure and even the kinetic data uncertain. The role of free-radical chain and molecular reactions in this process is still not fully understood. Various opinions and other information in the literature were reviewed briefly in an earlier Paper,[1] together with the report of detailed investigations on the thermal decomposition of many olefins.

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[1] M. Taniewski, *Proc. Roy. Soc.*, 1962, *A*, **265**, 519.

As an extension of earlier work on the thermal decomposition of a series of olefins[1,2] the pyrolysis of 4-methylpent-1-ene has been investigated. This compound was chosen because it was thought to be particularly suitable for a study of the controversial subject of the reactivity of allyl radicals, and of the part played by them in many decomposition processes (including propene-inhibited processes), and their ability to propagate chain reactions.

EXPERIMENTAL

The 4-methylpent-1-ene (95%; L. Light & Co.) was used without further purification apart from degassing and removal of the initial and final fractions. Its purity was checked by gas chromatography and conventional physicochemical methods. Nitric oxide was prepared by the reaction of ferrous sulphate with sodium nitrite in acid solution.[3]

The apparatus was similar to that previously used and specially designed for investigations of thermal processes by a static method.[1,2] A silica reaction vessel of volume 141 ml., covered internally with a carbon layer, was normally used. It was maintained at constant temperature in an electric furnace equipped with an electronic temperature controller and was fitted with an evacuation system, a pressure-measuring device, storage bulb, and facilities for introducing reactants and sampling products.

The course of the reaction was followed by observation of the pressure changes and by chromatography of the products. The rate was measured from the initial part of the pressure–time or concentration–time curves, when secondary processes can probably be still neglected. The initial rates were sufficiently reproducible. For gas chromatography (determination of the products up to C_4) a three-column apparatus employed previously was used.[4]

RESULTS AND DISCUSSION

The initial rates of the thermal decomposition of 4-methylpent-1-ene (r_0) were determined at four temperatures in the range 470—530° over the range of initial pressure (p_0) 25—200 mm. (occasionally to 300 or 400 mm. and at 450°). Over the whole investigated range the straight proportionality between the initial rate (rate of pressure change) and the initial pressure was observed (Figure 1); from this the reaction was found to be first-order under the experimental conditions, with the rate constants in Table 1. The reaction was accompanied by an approximate doubling of the number of moles ($\Delta p_\infty = p_\infty - p_0 \sim p_0$).

TABLE 1

Rate constants at different temperatures

Temp. (°c)	530	510	490	470
10^4k (sec.$^{-1}$)	46·6	25·0	11·7	5·0

Analysis of the products at different stages of the decomposition showed that the measurements of pressure change gave a reliable indication of the extent of reaction at least up to about 60—70% conversion; this proved the validity of Δp values as a measure of the rate. To illustrate this, the values of $-\Delta[C_6H_{12}]$ calculated indirectly from the analysis (all light products were determined by analysis, and the assumption was made that the only undetected higher component of the reaction mixture was unchanged 4-methylpent-1-ene) were compared with the corresponding Δp values. The result is shown in Figure 2 as a plot of conversion obtained from manometric measurements against conversion determined by analysis. The straight line corresponds to equality. The deviations are seen not to be too large, especially in view of possible analytical errors and the assumption made for calculations.

By plotting the rate constants in Table 1 as an Arrhenius plot (see Figure 3) the activation energy and frequency factor were obtained. The rate constant can be represented as

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[2] M. Taniewski, *Zeszyty Nauk. Politech. Slask.*, 55, *Chemia* 9, 1962.

[3] A. A. Blanchard, *Inorg. Synth.*, 1946, **2**, 126.

[4] M. Taniewski and G. Otremba, *Zeszyty Nauk. Politech. Slask.*, 106, *Chemia* 24, 1964, 217.

$k = 5{\cdot}0 \times 10^9 \exp(-44200/RT)$ sec.$^{-1}$. Analysis of the products clearly indicated that propene was the major primary product (cf. ref. 5). The other detected products were hydrogen, methane, ethane, ethylene, propane, butenes, and butadiene. The content of the major products of reaction in the gaseous reaction mixture was practically independent of conversion up to about 30—40% of the decomposition of 4-methylpent-1-ene for a given temperature and initial pressure. The yields of the products, if plotted against the percentage decomposition, give, naturally, a linear plot, thus indicating that they result from primary reactions. Only in the case of C_4 hydrocarbons was a slight negative curvature observed after a positive initial slope, suggesting that, although they are the primary products, they undergo further reaction. The yields of all other products relative to that of propene depend on the initial pressure and the reaction temperature. The increase in the initial pressure was accompanied by a considerable increase in the relative yield of propane and a slight increase in the yields of methane, ethane, and ethylene.

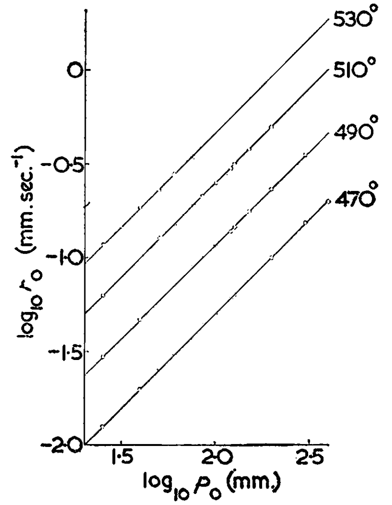

FIGURE 1. Double logarithmic plots of initial rate against 4-methylpent-1-ene initial pressure at various temperatures

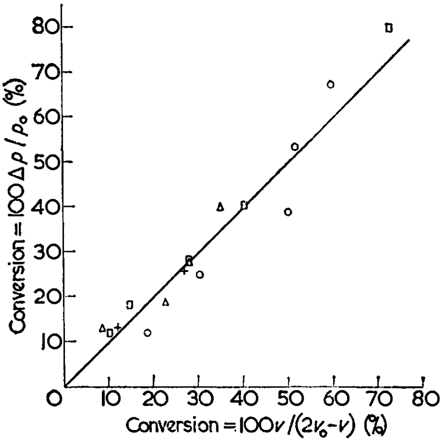

FIGURE 2. Plot of conversion obtained manometrically against conversion calculated from analytical data (v_0 = volume of the sample withdrawn, v = total volume of the detected reaction products). ○ 530°, □ 490°, △ 470°, + 450°

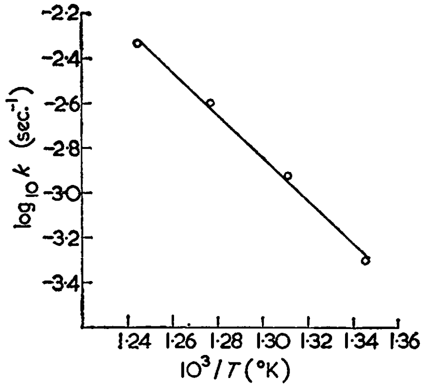

FIGURE 3. Arrhenius plot for the thermal decomposition of 4-methylpent-1-ene

The temperature-dependence may be illustrated by the data in Table 2, where the yields of various products relative to that of propene for 12—13% decomposition (p_0 =

100 mm.) at different temperatures are given. As shown in Table 2, relatively more propene and less of all other products is formed as the temperature is raised.

TABLE 2

Variation of relative yields of reaction products with temperature

Temp. (°C)	450	470	490	530
H_2	9·2	7·6	7·6	7·1
CH_4	31·5	29·5	25·0	18·7
C_2H_6	9·2	7·6	7·5	3·4
C_2H_4	21·0	19·7	17·0	12·7
C_3H_8	29·0	25·0	21·0	10·7
C_3H_6	100·0	100·0	100·0	100·0
1-C_4H_8	14·5	9·1	8·5	11·9
iso-C_4H_8	14·5	12·0	6·5	5·6
2-C_4H_8	—	—	—	0·5
C_4H_6	5·3	4·5	3·8	3·4
Molecular fraction of C_3H_6	0·43	0·47	0·51	0·57

The decomposition of 4-methylpent-1-ene in the presence of nitric oxide was also examined. The runs were carried out over the same range of temperatures and initial pressures as before, in the presence of various amounts of nitric oxide up to about 400 mm. In a study of the effect of nitric oxide on the initial rate of pressure change it was found that its inhibitory activity at low concentrations of nitric oxide was small, and so was its stimulatory activity when high concentrations of nitric oxide were used. Nitric oxide, although without much effect on the initial rate of pressure change, considerably affects the composition of the products at the initial stages of the decomposition, causing a rapid decrease in the yields of all by-products. Evidently, nitric oxide suppresses all processes leading to products other than propene. Table 3 gives some results of the influence of nitric oxide on the reaction products distribution.

As will be discussed in more detail, the observed kinetics and the composition of the reaction products provide evidence for a principally free-radical chain mechanism for the decomposition, although the possibility cannot be ruled out that some part of the decomposition occurs also by a molecular non-radical mechanism.

TABLE 3

Effect of nitric oxide on relative yields of reaction products at **470°** (p_0 = **100** mm.; conversion 14—15%)

Nitric oxide (mm.)	0	50	200	400
H_2	8·3	—	0·7	1·2
CH_4	29·5	7·2	7·2	6·1
C_2H_6	7·2	1·4	1·2	0·8
C_2H_4	19·2	12·3	10·7	13·9
C_3H_8	27·0	1·9	1·9	2·4
C_6H_6	100·0	100·0	100·0	100·0
1-C_4H_8	11·2	5·5	5·8	4·7
iso-C_4H_8	12·5	4·4	5·5	4·5
2-C_4H_8	0·5	—	—	—
C_4H_6	5·0	1·4	1·4	1·6
Molecular fraction of C_3H_6	0·46	0·75	0·74	0·74

The main reactions in the proposed free-radical mechanism, which accounts for the products and the observed kinetics, are (1)—(9). The initiation step (1) involves presumably a rupture of the weakest C–C bond in the β-position to the double bond, and therefore a split into allyl and isopropyl radicals. Isopropyl radicals thus formed partly decompose according to (2) or (3) and partly, like two other radicals formed in (2) and (3), attack the substate molecule, abstracting a hydrogen atom (reactions 4—6).

The proposed reactions for chain-propagating steps, (7) and (8), are based on the assumption that allyl radicals formed in (1) are sufficiently active to serve as chain-carriers and to abstract hydrogen from the molecule of C_6H_{12} (7). The reactivity of allyl, though undoubtedly lower than that of alkyl radicals, is quite sufficient to abstract hydrogen from the weak C–H bond α to the doubly bound carbon atom (and perhaps also from a more distant but tertiary C–H bond). The decomposition of $\mathrm{C_6H_{11}\cdot}$ radicals, (8), leads to allyl and propene, being thus the only product of that step. The combination in stage (9) terminates the chain process.

$$\mathrm{C_6H_{12}} \xrightarrow{k_1} \mathrm{C_3H_5\cdot + C_3H_7\cdot} \tag{1}$$

$$\mathrm{C_3H_7\cdot} \xrightarrow{k_2} \mathrm{C_2H_4 + CH_3\cdot} \tag{2}$$

$$\mathrm{C_3H_7\cdot} \xrightarrow{k_3} \mathrm{C_3H_6 + H\cdot} \tag{3}$$

$$\mathrm{H\cdot + C_6H_{12}} \xrightarrow{k_4} \mathrm{H_2 + C_6H_{11}\cdot} \tag{4}$$

$$\mathrm{CH_3\cdot + C_6H_{12}} \xrightarrow{k_5} \mathrm{CH_4 + C_6H_{11}\cdot} \tag{5}$$

$$\mathrm{C_3H_7\cdot + C_6H_{12}} \xrightarrow{k_6} \mathrm{C_3H_8 + C_6H_{11}\cdot} \tag{6}$$

$$\mathrm{C_3H_5\cdot + C_6H_{12}} \xrightarrow{k_7} \mathrm{C_3H_6 + C_6H_{11}\cdot} \tag{7}$$

$$\mathrm{C_6H_{11}\cdot} \xrightarrow{k_8} \mathrm{C_3H_6 + C_3H_5\cdot} \tag{8}$$

$$\mathrm{C_3H_5\cdot + C_6H_{11}\cdot} \xrightarrow{k_9} \text{Products} \tag{9}$$

The amount of information on the behaviour of the allyl radical and its reactivity is limited. The highly resonance-stabilised allyl radical has been widely assumed to be relatively unreactive and not capable of acting as a chain carrier.[6,5] The low reactivity of the allyl radical is said to be caused by the electron-delocalisation process occurring on formation of the radical. The resonance or delocalisation energy of allyl radical has been studied.[7,8] The inhibitory power of propene in certain hydrocarbon decompositions has often been connected with the substitution of reactive radicals, like alkyls, by comparatively stable and unreactive allyl in the process of hydrogen-abstraction from propene.

In recent years evidence on the ability of allyl to abstract hydrogen from certain other molecules at temperatures not lower than about 500° has been provided. Thus, McNesby and Gordon [9] and Gordon, Smith, and McNesby [10] observed the abstraction of hydrogen by allyl radicals from cyclopentane. The authors also expressed the idea that allyl radicals are chain-carriers in propene-inhibited reactions. Bryce and Ruzicka,[11,12] studying the thermal decomposition of diallyl and the reactions of allyl with butenes, propene, ethylene, and butane, showed that under the experimental conditions allyl is capable of abstracting hydrogen from hydocarbons and of adding to olefinic double bonds. Wojciechowski and Laidler [13,14] based on such a view their scheme of the propene-inhibited decomposition of ethane, and McKenny, Wojciechowski, and Laidler [15] that of dimethyl ether.

It is believed that the results of the present work clearly indicate that allyl is capable of abstracting hydrogen from 4-methylpent-1-ene, and in its decomposition allyl is the principal chain-carrier. Thus, the ability of allyl to abstract hydrogen from certain hydrocarbons seems to be confirmed.

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[5] N. N. Semenov, " Some Problems of Chemical Kinetics and Reactivity," Pergamon Press, London, 1958.

[6] E. W. R. Steacie, " Atomic and Free Radical Reactions," Reinhold, New York, 1954.

[7] C. A. Coulson, *Proc. Roy. Soc.*, 1938, *A*, **164**, 383.

[8] J. L. Bolland and G. Gee, *Trans. Faraday Soc.*, 1946, **42**, 244.

[9] J. R. McNesby and A. S. Gordon, *J. Chem. Phys.*, 1959, **31**, 853.

[10] A. S. Gordon, S. R. Smith, and J. R. McNesby, *J. Amer. Chem. Soc.*, 1959, **81**, 5059.

[11] D. J. Ruzicka and W. A. Bryce, *Canad. J. Chem.*, 1960, **38**, 827.

[12] W. A. Bryce and D. J. Ruzicka, *Canad. J. Chem.*, 1960, **38**, 835.

[13] B. W. Wojciechowski and K. J. Laidler, *Canad. J. Chem.*, 1960, **38**, 1027.

[14] K. J. Laidler and B. W. Wojciechowski, *Proc. Roy. Soc.*, 1960, *A*, **259**, 257.

[15] D. J. McKenney, B. W. Wojciechowski, and K. J. Laidler, *Canad. J. Chem.*, 1963, **41**, 1993.

The reaction scheme proposed above does not include, for simplicity, some other plausible reactions such as isomerisation of radicals, disproportionation reactions, addition of free radicals to the olefinic bond of olefins, other types of decomposition of the $C_6H_{11}\cdot$ radical, etc. Thus, according to the mechanism, whenever an ethylene molecule is produced a methyl radical is formed [reaction (2)], and this may give rise to a methane molecule by reaction (5). The rates of formation of ethylene and methane should therefore be approximately equal. Analysis, however, reveals that less ethylene than methane is actually formed; this can perhaps be ascribed to some additional ways in which methyl radicals can be formed, such as decomposition of $C_6H_{11}\cdot$ into methylbutadiene (pentadiene) and methyl, though such reactions are scarcely significant under the experimental conditions employed. Ethane may be formed, *e.g.*, by combination of methyl radicals, cross-disproportionation of methyl and isopropyl radicals, etc. But-1-ene is probably produced by combination of methyl and allyl radicals. The ways in which isobutene and butadiene can be formed are less clear, though they are undoubtedly, at least in part, products of some radical reactions, as is shown below by the decomposition in the presence of nitric oxide.

When the steady-state treatment is applied to the above scheme, the following expressions for the radical concentrations are obtained.

$$[C_3H_7\cdot] = k_1[\mathrm{RH}]/(k_2 + k_3 + k_6[\mathrm{RH}])$$

$$[CH_3\cdot] = k_1k_2/k_5(k_2 + k_3 + k_6[\mathrm{RH}])$$

$$[H\cdot] = k_1k_3/k_4(k_2 + k_3 + k_6[\mathrm{RH}])$$

$$[C_3H_5\cdot] = (k_1k_8/k_7k_9)^{\frac{1}{2}}$$

$$[C_6H_{11}\cdot] = (k_1k_7/k_8k_9)^{\frac{1}{2}}[\mathrm{RH}]$$

The rate of the overall reaction is given by

$$V = -\mathrm{d}[\mathrm{RH}]/\mathrm{d}t \sim (k_1k_7k_8/k_9)^{\frac{1}{2}}[\mathrm{RH}]$$

the reaction being of the first order.

Under the mechanism proposed and the kinetics evaluated, the overall activation energy may be calculated from the activation energies of the elementary reactions as follows:

$$E = \tfrac{1}{2}(E_1 + E_7 + E_8 - E_9).$$

This leads to the activation energy of the abstraction of hydrogen by allyl (7):

$$E_7 = 2E - (E_1 + E_8 - E_9).$$

The activation energy of a radical recombination process (9) may be assumed to be zero. The value of E_1 is estimated to be equal to the bond energy C_3H_5–iso-C_3H_7 quoted[6] as 54·5 kcal. mole^{-1}. The value of E_8 is unfortunately not available, but on the basis of the analysis of certain thermodynamic functions it is estimated to be about 22 kcal. mole.$^{-1}$. Using these values and the experimental value of E equal to 44·2 kcal. mole^{-1}, the activation energy E_7 was calculated to be about 12 kcal. mole^{-1}. This value is higher than those usually quoted for the hydrogen abstraction by alkyls, which is not unexpected in view of the much lower reactivity of allyl radicals. At the same time, this value is considerably smaller than that reported earlier[10] for abstraction of hydrogen atoms from cyclopentane (32 kcal. mole^{-1}), which is to be expected considering that cyclopentane, unlike 4-methylpent-1-ene, does not possess the weak C–H bonds α to the doubly bound carbon atom, or the weak C–H bond with the tertiary hydrogen.

Hydrogen-abstraction from cyclopentane by allyl is endothermic by about 17 kcal. mole^{-1} [$D(C_3H_5{-}H) = 77$ and $D(C_5H_{10}{-}H) = 94$ kcal. mole^{-1}]. In contrast, hydrogen-abstraction from 4-methylpent-1-ene by allyl (at least abstraction of a secondary hydrogen atom adjacent to the doubly bound carbon) is presumably slightly exothermic, as the C–H bond strength with the primary hydrogen atom in $CH_2{:}CH{\cdot}CH_2{-}H$ should be somewhat higher than the C–H bond strength with the secondary hydrogen atom in a similarly built $CH_2{:}CH{\cdot}CHPr^i{-}H$. It is estimated that this reaction is exothermic by about 5 kcal. mole^{-1} [assuming $D(C_6H_{11}{-}H)$ to be approximately 72 kcal. mole^{-1}].

It may be of interest to mention that application to this case of the approximate relationship between heat of reaction and the activation energy quoted by Semenov [5] leads to the value of 10·25 kcal. mole^{-1} for E_7, in satisfactory agreement with the value obtained above.

The kinetics of the chain reaction proposed lead to the increase in chain length as the temperature is raised. As the only product of the chain-propagation step according to the scheme proposed is propene, its content in the reaction products should rise with rise of temperature. Remarkably, this is exactly what is found experimentally (cf. Table 2).

The presence of nitric oxide only very slightly affects the initial rate of decomposition of 4-methylpent-1-ene, which can be satisfactorily explained on the basis of the proposed mechanism, if it is postulated that a chain-carrier, *i.e.*, the allyl radical, does not react at all or reacts only very reluctantly with nitric oxide. Such views about the ineffectiveness of the reaction between nitric oxide and electronically stabilised radicals like allyl were put forward by Bryce and Ruzicka.[12]

On the other hand, the fact that nitric oxide can react easily with the active radicals, like hydrogen atoms or alkyl radicals, should cause the suppression of reactions (4), (5), and (6), leading to H_2, CH_4, and C_3H_8, respectively. In full agreement with this prediction, it was established by analysis that under the experimental conditions the yields of H_2 and C_3H_8 (as well as C_2H_6 and C_4H_6) fall off in the presence of nitric oxide almost to zero (cf. Table 3). Small amounts of hydrogen which reappeared when very large quantity of nitric oxide were used may be attributed to the additional initiation step (1′) which is estimated to have an activation energy of about 25 kcal. mole^{-1}.

$$NO + C_6H_{12} \longrightarrow HNO + C_6H_{11}\cdot \qquad (1')$$

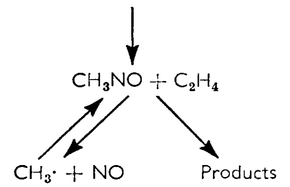
$$HNO \longrightarrow H\cdot + NO$$

The yields of all other products, such as CH_4, C_2H_4, and C_4, relative to that of propene fall off considerably in the presence of nitric oxide, though not to zero.

The presence of some methane in the reaction products may be regarded as evidence for the presence of some methyl radicals even in the presence of nitric oxide. This conclusion seems to be supported by the presence of but-1-ene being probably formed in the reaction

$$CH_3\cdot + C_3H_5\cdot \longrightarrow 1\text{-}C_4H_8$$

One of several plausible schemes which may be offered to explain the presence of CH_4 and C_2H_4 and the absence of C_3H_8 and H_2 in the reaction products formed in the presence of nitric oxide is



It was found that nitric oxide only very slightly affected the initial rate of pressure change but a pronounced increase in rate of pressure change at higher conversions resulted. Figure 4 shows typical pressure–time curves for decomposition of 100 mm. 4-methylpent-1-ene in the absence and in the presence of various amounts of nitric oxide. The shape of the pressure–time curves obtained in the absence of nitric oxide and the comparison of various partial reaction times evaluated from them may imply that the decomposition, which is clearly of the first order for low conversions, changes its order to higher values as more extensive reaction occurs. This apparent change of order should, however, be attributed to the increasing importance of secondary reactions which lead to the actual decrease in rate (self-inhibition) or to the decrease in volume by formation some non-volatile products. Such reactions may involve the propene molecule, *e.g.*,

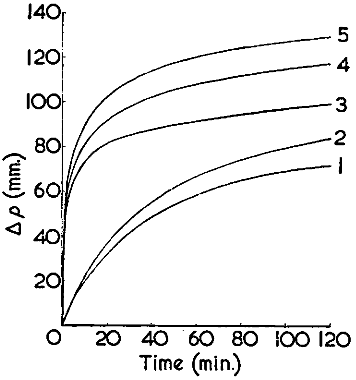


FIGURE 4. The pressure–time curves for the decomposition of 100 mm. 4-methylpent-1-ene. 1, 470°, without NO; 2, 470°, 100 mm. NO; 3, 530°, without NO; 4, 530°, 100 mm. NO; 5, 530°, 200 mm. NO

$$C_6H_{11}\cdot + C_3H_6 \longrightarrow C_6H_{12} + C_3H_5\cdot \qquad (-7)$$

$$C_3H_5\cdot + C_3H_6 \longrightarrow C_6H_{11}\cdot \qquad (-8)$$

$$C_3H_5\cdot + C_3H_6 \longrightarrow \text{higher products} + \text{radical} \qquad (10)$$

In the presence of nitric oxide the rate of pressure change for higher extent of reaction is considerably increased. As a result, in the presence of nitric oxide the process of complete decomposition is accompanied by a much greater increase in volume.

The stimulation of the secondary decomposition of such primary products as propane, higher products, even propene (at least to a small extent), and others is assumed to be responsible for the phenomenon observed. This conclusion was next confirmed directly by analysis of the products of decomposition of 4-methylpent-1-ene at very high conversions in the absence and in the presence of nitric oxide. In the presence of nitric oxide more methane and hydrogen, but much less propane and somewhat less propene and ethane, were found.

It is obvious from the evidence cited that free radicals play an important role in the decomposition of 4-methylpent-1-ene. All the evidence strongly suggests that the role of the allyl radical in this process is of particular importance, and, though the reaction mechanism cannot yet be regarded as definitely established, the scheme postulated above accounts satisfactorily for the observed kinetics and analytical results both in the absence and in the presence of nitric oxide.

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