75. *The Kinetics of the Thermal Decomposition of Olefins. Part II.**

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A comparative study has been made of the thermal decomposition of the following olefins in a static system : but-1-ene, pent-1-ene, hex-1-ene, hept-1-ene, but-2-ene, *iso*butene, 2-methylbut-1-ene, 3-methylbut-1-ene. Analyses of the products of the reaction for some of them were made by taking samples at different times. The observed pressure increase was shown to be a measure of the olefin decomposed, for at least the first part of the decomposition. The decomposition is in each case a first-order reaction, and the activation energies have been determined. *iso*Butene has been studied in more detail and a reaction mechanism is proposed. A brief study of the pyrolysis of ethylene has shown that over the range 600—800° polymerization and decomposition occur together, the latter predominating at higher temperatures.

Part I of this series (Ingold and Stubbs, *loc. cit.**) has dealt with the thermal decomposition of propylene in a static system. The decomposition was found to be a homogeneous first-order reaction with activation energy 57·1 kcal./g.-mol. The present paper extends the investigation to the olefins named in the summary.

Several investigations of the pyrolysis of higher olefins have been carried out but mostly in flow systems or under conditions of temperature and pressure different from those used in the static apparatus in the present work. Many of these investigations refer to the three butenes (Hurd and Spence, *J. Amer. Chem. Soc.*, 1929, **51**, 3566; Hurd, *J. Ind. Eng. Chem.*, 1934, **26**, 50; Tropsch, Parrish, and Egloff, *Ind. Eng. Chem.*, 1936, **28**, 581; Hurd and Blunk, *J. Amer. Chem. Soc.*, 1937, **59**, 1869; Steacie and Shane, *Canadian J. Res.*, 1938, **16**, *B*, 210; Rice and Haynes, *J. Amer. Chem. Soc.*, 1948, **70**, 964; Rice and Wall, *ibid.*, 1950, **72**, 3967), and to the pentenes (Gorin, Oblad, and Schmuck, *Ind. Eng. Chem.*, 1946, **38**, 1187; Hepp and Frey, *ibid.*, 1948, **41**, 827).

A comparative study of the series of olefins is interesting in that it provides information about the way in which the decomposition rate varies in the series of straight-chain Δ^1-olefins or in a group of isomeric olefins, knowledge of the products formed and their proportions giving an indication of the reaction mechanism. Moreover, since the thermal decomposition of a paraffin gives a lower paraffin and an olefin, for a complete interpretation of the paraffin results it is important to know the relative stability of various olefins. It is also of interest to compare behaviour in the paraffin and the olefin series.

EXPERIMENTAL

The apparatus and technique have already been described (Stubbs and Hinshelwood, *Proc. Roy. Soc.*, 1950, *A*, **200**, 458). The following olefins were standard samples from the National Bureau of Standards (U.S.A.) : Pent-1-ene, hex-1-ene, 2-methylbut-1-ene, 3-methylbut-1-ene. Hept-1-ene was a specially pure sample supplied by Imperial Chemical Industries Limited, Billingham.

The three butenes were prepared as follows : But-1-ene was prepared by the action of alcoholic potash on *n*-butyl iodide. The but-1-ene formed was condensed in a trap cooled with liquid air, then fractionated, the middle fraction only being collected. Its purity was tested by infra-red spectroscopy by Dr. R. L. Williams and Dr. H. W. Thompson and found to be 98 ± 2%. But-2-ene, prepared by dehydration of *sec.*-butyl alcohol with phosphoric oxide, was fractionated, and its purity, tested by infra-red spectrometry and mass spectrometry, was at least 95%. *iso*Butene was made by the dehydration of *tert.*-butyl alcohol with anhydrous oxalic acid at 80° and fractionated. Its purity was tested in the mass spectrometer.

Analyses of the gaseous reaction products were made in one of the two ways :

(1) By conventional methods in a Bone and Wheeler apparatus. Propylene and higher olefins were absorbed in 82·4% sulphuric acid (Hurd and Spence, *J. Amer. Chem. Soc.*, 1929, **51**, 3353), and ethylene in a saturated solution of mercuric acetate. Saturated hydrocarbons

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* Part I, *J.*, 1951, 1749.

were determined by explosion with oxygen. Carbon dioxide was used as reference gas, a known amount being introduced into the reaction vessel together with the olefin. In this way, the absolute amount of product formed could be calculated. In the case of olefins that are liquid at room temperatures, the gaseous product and unchanged olefin were passed through a trap cooled with solid carbon dioxide to condense out the olefin at the moment of taking the sample, before introducing it into the Bone and Wheeler apparatus.

(2) By mass-spectrograph analysis. This work was carried out by Dr. C. J. Danby and Mr. I. A. Henderson. Helium was used as reference gas in this case. Difficulties were encountered, in particular the formation of higher polymers which interfered with the accurate estimation of lower olefins. The technique will be reported in detail elsewhere.

General Form of Δp*–Time Curves.*—With most of the higher olefins the initial portion of the Δp–time curve (where Δp is the observed increase of pressure in mm. of mercury) is a straight line passing through the origin, and there is the normal decrease in rate as the reaction comes to an end. Estimation of the initial rate presents no difficulty.

With *iso*butene and but-2-ene, and in some of the experiments on 2-methylbut-1-ene, and 3-methylbut-1-ene, there is at first a short time during which Δp is inappreciable and after which the slope of the curve rises quickly to a maximum, subsequently decreasing as the reaction comes to an end. This type of Δp–time curve is also observed with propylene. For comparative purposes the rate is taken as the maximum slope of the curve.

It now remains to consider how far the Δp–time curves give a definite measure of the rate at which olefin is used.

It was found for propylene over a range of different temperatures and pressures (Ingold and Stubbs, *loc. cit.*) that, for at least the first half of the reaction, the amount of propylene used is, after a short initial period, proportional to Δp.

It will now be shown that for *iso*butene Δp is in fact also a definite measure of the olefin consumed, *i.e.*, the plot of *iso*butene used against Δp is a straight line. It will also be shown that plots of the products formed (CH_4, C_2H_4, H_2, etc.) against Δp all yield straight lines. These do not pass exactly through the origin, some olefin initially being used without pressure change, but after quite a short interval, the rate of change of Δp becomes a reasonable measure of the rate of consumption of the olefin itself.

For the olefins above C_4 the amount of olefin used cannot be determined, but the plots of products formed against Δp all lie on straight lines. It is inferred therefore that for the higher olefins also the olefin consumed plotted against Δp would also yield a straight line, *i.e.*, that Δp is a reasonable measure of the reaction rate.

Order of the Reaction.—The variation of rate (from Δp–time curves) with initial olefin pressure is recorded for various temperatures in Table 1, and the results for some typical olefins are plotted in Fig. 1. In all cases the reactions are of the first order down to quite low pressures, where the characteristic transition towards the second-order occurs, in accordance with what might be expected from the process of collisional activation.

TABLE 1. *Variation of rate with pressure.**

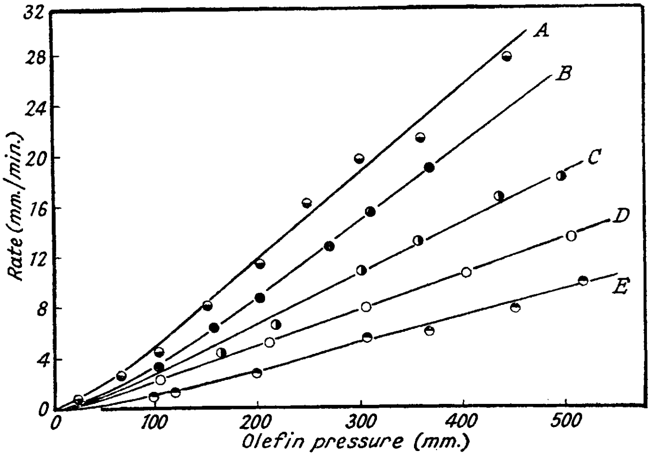
But-1-ene, 540°	p_0	53	98·5	196·5	297·8	398	503·5			
	rate	1·2	2·1	4·8	7·7	11	13·8			
But-2-ene, 540°	p_0	93·5	117·5	198·5	305	364	449	518·5		
	rate	1·3	1·35	2·8	5·7	6·2	8·0	10·0		
*iso*Butene, 580°	p_0	52·5	116	206	298	361	421	483	514·5	
	rate	1·1	2·9	6·3	9·6	12·0	14·0	17·0	18·5	
Pent-1-ene, 480°	p_0	102·5	209·5	306·5	420·8	504				
	rate	2·5	5·7	8·2	10·8	13·6				
2-Methylbut-1-ene, 530°	p_0	100	163·5	216·5	300	354	435	496		
	rate	3·3	4·6	6·6	11·0	13·3	17·0	18·5		
3-Methylbut-1-ene, 520°	p_0	67	101	154	200·5	269	308·5	366·5		
	rate	2·9	3·5	6·5	8·8	12·8	15·5	19·0		
Hex-1-ene, 470°	p_0	36·5	99	149	202·5	252	301	353	412	
	rate	0·75	2·8	4·5	6·2	8·0	9·5	11·5	13·0	
Hept-1-ene, 470°	p_0	23·5	66	102·5	150	201·5	248	299·5	360	446
	rate	0·85	2·8	4·7	8·3	11·5	16·5	20·0	21·5	28

* All pressures (p_0) measured in terms of mm. of Hg. All rates are recorded as mm. of Hg/min.

It is of interest to see whether the Δp–time curves follow a first-order equation or whether the first-order behaviour is only shown by the initial rates.

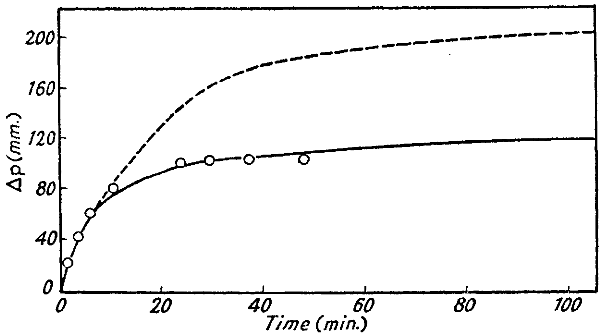
For most of the olefins the actual relation between Δp and olefin consumed is not known. In the first-order equation $\ln a/(a - x) = kt$ the simplest assumption would be $x = \Delta p$ but, as Table 2 shows, for several olefins Δp_∞ is less than the initial pressure. If, however, we suppose $x = m\Delta p$, the values of m can be determined from the experimental curve and are recorded in the last column of Table 2. Fig. 2 shows for a typical case how with these values of m a theoretical first-order curve and an experimental curve agree over a considerable proportion of the reaction.

FIG. 1. *Rate–pressure curves for various olefins.*



A, Hept-1-*ene,* 470°. *B,* 3-*Methylbut*-1-*ene,* 520°. *C,* 2-*Methylbut*-1-*ene,* 530°. *D, Pent*-1-*ene,* 450°. *E, But*-2-*ene,* 540°.

FIG. 2. Δp–*time curve for the decomposition of* 200 *mm. of but*-1-*ene at* 560°.



Full curve : observed Δp.
○, *Theoretical points for first-order reaction ;* $x = 2\Delta p$.
Broken curve : Theoretical curve for first-order reaction ; $x = \Delta p$.

It has not been possible to fit results for hept-1-ene to such a curve, probably because of the secondary decomposition of the products; nor can the Δp–time curves for but-2-ene and *iso*butene be adjusted to a first-order equation because these curves show a sigmoid form.

TABLE 2. *Values of* $\Delta p_\infty/p_0$ *for different olefins.*

	$\Delta p_\infty/p_0$	Temp.	m		$\Delta p_\infty/p_0$	Temp.	m
Hept-1-ene	1·38	510°	—	But-2-ene	0·57	540	—
Hex-1-ene	0·97	500	1·2	2-Methylbut-1-ene	0·77	530	1
Pent-1-ene	0·80	500	1·6	3-Methylbut-1-ene	0·80	520	1·5
But-1-ene	0·62	560	2				

Activation Energy.—The activation energies for all the olefins are recorded in Table 3, together with the conditions in which they have been determined. Within the error of the experiments, the activation energy does not vary with the initial pressure. This behaviour is in contrast with that shown by the normal paraffins (Ingold, Stubbs, and Hinshelwood, *Proc. Roy. Soc.*, 1950, *A*, **203**, 487).

Effect of Added Gases.—A number of experiments have been carried out in which nitric oxide or lower olefins have been added to the olefin under study to see whether or not they show an inhibitory effect. The results are collected in Table 4.

TABLE 3. *Activation energies.*

	Range of temp.	Press., mm.	kcal./ g.-mol.		Range of temp.	Press., mm.	kcal./ g.-mol.
But-1-ene	490—600°	100	66·4	2-Methylbut-1-ene	520—570	100	62·8
But-2-ene	540—590	100	57·4			300	61·5
		300	55·6	3-Methylbut-1-ene	510—570	100	65·0
*iso*Butene	580—630	100	53·3			300	61·8
Pent-1-ene	430—530	100	53·1	Hex-1-ene	460—530	100	53·3
		300	54·6	Hept-1-ene	450—510	100	49·0

TABLE 4. *Effect of added gases on the decomposition rate of various olefins.*

	Nitric oxide	Ethylene	Propylene	But-1-ene
Propylene	acceln.	—	—	—
But-1-ene	acceln.	slight decrease	none	—
But-2-ene	acceln.	—	—	—
*iso*Butene	none	—	—	—
Pent-1-ene	none	slight decrease	slight decrease	—
2-Methylbut-1-ene	none	slight decrease	slight decrease	—
3-Methylbut-1-ene	slight acceln.	slight decrease	slight decrease	none
Hex-1-ene	none	none	none	none
Hept-1-ene	none	none	none	none

Analytical Results.—Table 5 shows the results of the analyses (carried out with a Bone and Wheeler apparatus) of samples taken at different times during the decomposition of 200 mm. of hex-1-ene and of hept-1-ene. For both, the plot of the amount of each of the different products against time shows the same general shape as the Δp–time curve.

TABLE 5. *Reaction products from hex-*1*-ene and hept-*1*-ene.* (*Initial press.,* 200 *mm.*).*

	Hex-1-ene, 500°				Hept-1-ene, 510°			
Total press. in reaction vessel before sampling	225	250	280	300	225	250	275	300
Δp	25	50	80	100	25	50	75	100
Press. of sample	43	72·5	113	152	39	70	105	111
Ethylene	13	20	34	48	18	24	44	39
Other olefins	19	28	42	54	7	20	27	32
Saturated hydrocarbons + hydrogen ...	11	25·5	37	50	14·5	26	34	40
Contraction after explosion	28·5	58	69·5	104	28	50	66	68
CO_2 from explosion	22	55	51	77	20	38	43	49

TABLE 6. *Reaction products from* iso*butene at* 580° (*initial press.,* 200 *mm.*).*

Δp	H_2 formed	CH_4 formed	C_3H_6 formed	C_2H_4 formed	*iso*Butane formed	*iso*Butene reacted	Other products formed	Con-densed	C_3H_8 formed
2	2·44	4·6	3·17	0	1·17	32	1·2	30	0
5	4·17	6·77	4·67	3·74	1·64	35·7	3	24	0
10	6·30	11·2	6·75	1·89	2·52	35	7	20	0
20	9·92	19·5	9·88	3·87	3·68	64	14	44	0
40	19·4	38·1	14·7	13·1	5·17	104	30	67	0

* All pressures are expressed in mm. of mercury.

In Table 6 are included the results of analyses (carried out in a mass spectrometer) of samples taken at different times from the decomposition of 200 mm. of *iso*butene. Similar analyses from experiments made with the addition of 20 mm. of nitric oxide have been made, and it has been shown that the products of the pyrolysis of *iso*butene have the same composition, with or without nitric oxide.

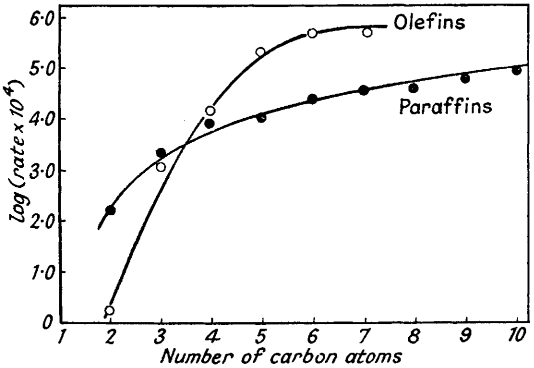
DISCUSSION

Number of Carbon Atoms.—Owing to the various difficulties described previously, the analytical results are unfortunately not precise enough to define the exact reaction mechanism for the whole series of olefins. For propylene it has been shown that the reaction proceeds by a number of steps, and, as will be discussed later, the results for *iso*butene indicate a similar mechanism. For the other olefins also the reaction will probably go by a series of steps. In general, in such a case the velocity constant and activation energy measured will be a function of the velocity constants of the different steps. In the present example, however, it is difficult to account for a *first-order* reaction leading to considerable polymerization, unless the rate is chiefly governed by a primary step involving decomposition. If this is so, then the measured activation energy will refer to this step.

Fig. 3 shows the plot of log rate against the number of carbon atoms for the series of straight-chain Δ^1-olefins, together with a similar plot for the nitric oxide-inhibited decomposition of the normal paraffins (for comparison the nitric oxide-inhibited reaction of the latter must be used, since this is believed to be the molecular decomposition process). It is seen that for the olefins, there is initially a much more rapid increase of rate with the number of carbon atoms than for the paraffins.

The curves cross between C_3 and C_4 and it is interesting to consider the reason for this. Ethylene and propylene decompose more slowly than the corresponding paraffins, and neither has a C–C bond β to the double bond. It has been stated as a general rule that when there is a doubly bonded carbon atom in a molecule, the bonds in the α-position to this bond are stronger than normal, whereas those in the β-position are weaker (Rice and Rice, " The Aliphatic Free Radicals "). Thus the absence of the β-bond in ethylene and propylene would mean a bigger activation energy for the initial step and a consequent diminution in the rate. The higher olefins having a C–C bond in the β-position to the double bond, it might be argued that the decomposition rate would be greater than with the corresponding paraffin. This explanation is however doubtful, since Stevenson's results (Steacie, " Atomic and Free Radical Reactions ") on the α-bonds in olefins do not appear to show a strengthening compared with the bond in the corresponding paraffin.

FIG. 3. *Relative reaction rates for members of the normal paraffin series and straight-chain* Δ^1*-olefins* (530°; p_0 = 100 *mm.*).



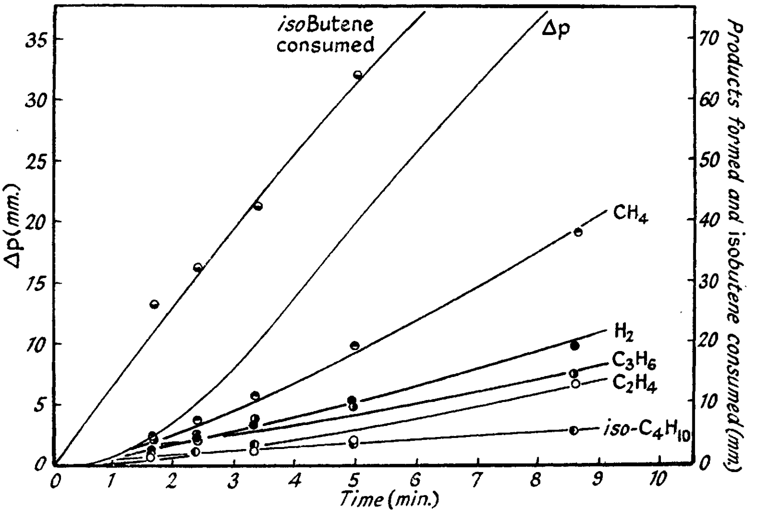
Activation Energy.—An inspection of the activation-energy values in Table 3 makes possible a certain classification of the olefins. If *iso*butene is considered as a substituted propylene, we can say that the substitution of a $C_{(2)}$-hydrogen atom by a methyl group diminishes the activation energy (propylene, 57; *iso*butene, 53). Comparing now but-1-ene with its 2- and its 3-methyl-substituted compounds, it appears that the substitution of the $C_{(2)}$-hydrogen atom of but-1-ene by a methyl group produces a diminution of the activation energy similar to that observed in propylene and *iso*butene (but-1-ene, 66·4; 2-methylbut-1-ene, 62). On the other hand, the substitution of a $C_{(3)}$-hydrogen atom of but-1-ene by a methyl group produces a very small diminution of the activation energy (but-1-ene, 66·4; 3-methylbut-1-ene, 64). Comparison of the two linear butenes shows that but-2-ene has a lower activation energy (but-1-ene, 66·4; but-2-ene, 56·5).

Consideration of the linear Δ^1-olefins from butene upwards shows a decrease in activation energy as the series is ascended. For a particular olefin, however, the activation energy does not vary with the pressure, in contrast to the behaviour observed with the nitric oxide-inhibited decomposition of the normal paraffins.

Number of Degrees of Freedom.—According to conventional methods the minimum number of degrees of freedom (n) among which E must be distributed to account for the absolute rate, has been calculated for each olefin, and the results are collected in Table 7. They have all been calculated for 200 mm. pressure, because in this region of pressure the transition from the first to the second order appears to be in progress. The molecular diameter has been assumed to be the same for all the olefins, *viz.*, 5×10^{-8} cm.

In the calculation of the absolute velocity (molecules per c.c. and sec.) the ratio of Δp to amount of olefin used has been assumed equal to two. In the case of *iso*butene, analysis has proved this to be true. Direct determination for the other olefins has not been possible although the values of m in Table 2 are between 1 and 2. In any case, a great variation of m is necessary to change the number of degrees of freedom required to account for the observed rates. The values in Table 7 can therefore be accepted as very probable ones, and the number of degrees of freedom is seen in every case to be plausible, having regard to the formulæ of the olefin molecules.

FIG. 4. *Thermal decomposition of* 200 *mm. of* iso*butene at* 580°; *variation of reaction products with time.*



Mechanism of Reaction.—The analytical results for the higher olefins studied in the present work (hex-1-ene and hept-1-ene) are not complete enough to justify detailed conclusions regarding the mechanism of decomposition. Consideration of this will therefore be restricted to *iso*butene, where mass-spectrometric analyses have provided fuller information.

According to the experimental results in Table 6, in the decomposition of *iso*butene at 580°, the products are to a considerable extent polymers, most of which condense on sampling. Up to 50% of decomposition, less than 47% of the carbon atoms and less than 32% of the hydrogen atoms can be accounted for, the rest being lost by condensation.

TABLE 7. *Degrees of freedom required to account for reaction rate.*

Olefin	Temp.	n	Olefin	Temp.	n	Olefin	Temp.	n
But-1-ene.........	530°	9	Pent-1-ene	470°	5	Hex-1-ene	470°	5—6
But-2-ene.........	530	4	2-Methylbut-1-ene...	530	8	Hept-1-ene	470	4
*iso*Butene.........	580	2	3-Methylbut-1-ene...	530	9			

The Δp–time curve for *iso*butene (Fig. 4) shows an upward curvature before the maximum rate is obtained, and it appears that, as for propylene, there are at first reactions of *iso*butene without change of pressure, giving intermediate compounds which subsequently decompose.

It is important to know the relative amounts in which products are produced at zero time. For this purpose, the values of Table 8 have been calculated from the experimental values of Table 6 and the extrapolation to zero time gives the values of the last row. All products have been referred to methane, since this does not decompose at 580°, whereas propylene and *iso*butane decompose appreciably, producing the variation with time that is observed in the ratios given in Table 8.

TABLE 8. *Ratios of analytical products.*

Time	CH_4/C_3H_6	CH_4/C_2H_4	CH_4/H_2	CH_4/*iso*Butane	H/C (cond. prod.)
1′ 36″	1·4	—	1·8	3·9	1·8
2′ 18″	1·4	1·8	1·7	4·1	1·7
3′ 18″	1·6	5·9	1·8	4·4	1·7
4′ 48″	1·9	5·0	1·9	5·3	1·6
8′ 30″	2·5	2·9	1·9	7·3	1·5
0 (extr.)	1	7·5	1·85	3·0	1·9

Since there has been no analysis of the condensed products themselves, only a tentative mechanism can be proposed. Any mechanism for the decomposition of *iso*butene under the conditions of this work must take into account three factors: (1) More than 50% of the *iso*butene used forms polymers; (2) a "lag" in the Δp–time curve; (3) the extrapolated relations of Table 8.

These facts being considered in relation to the mechanism already proposed for propylene, there are two different possibilities for the primary breaking of the molecule of *iso*butene that account for them, *viz.*, the breaking into two radicals:

$$(CH_3)_2C{:}CH_2 \longrightarrow CH_3 + C_3H_5 \quad . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

or the breaking and transfer of a hydrogen atom by molecular rearrangement:

$$(CH_3)_2C{:}CH_2 \longrightarrow CH_4 + C_3H_4 \quad . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

In case (1) subsequent steps will be the immediate reaction of each radical with a molecule of *iso*butene, giving methane and propylene respectively:

$$(CH_3)_2C{:}CH_2 + CH_3 \longrightarrow CH_4 + C_4H_7$$
$$(CH_3)_2C{:}CH_2 + C_3H_5 \longrightarrow CH_3{\cdot}CH{:}CH_2 + C_4H_7$$

If we assume that the two C_4 radicals polymerise to form a C_8 compound, these steps would be summed up as follows:

$$3\ \textit{iso}\text{Butene} \longrightarrow CH_4 + C_3H_6 + C_8H_{14} \quad . \; . \; . \; . \; . \quad (3)$$

If we suppose that the first step is (2), the molecule C_3H_4 can abstract two atoms of hydrogen from two molecules of *iso*butene, and the overall sum of the steps gives the same reaction (3): $(CH_3)_2C{:}CH_2 + C_3H_4 \longrightarrow C_4H_7 + C_3H_5$; $(CH_3)_2C{:}CH_2 + C_3H_5 \longrightarrow C_4H_7 + CH_3{\cdot}CH{:}CH_2$.

The extrapolated values in Table 8 justify equation (3): methane and propylene can be considered as the stable primary products in equal proportion. Ethylene is a product in the decomposition of propylene, and *iso*butane is obviously a secondary product formed by hydrogenation of *iso*butene. Hurd and Blunk (*loc. cit.*) found under very similar conditions that the primary products were methane and propylene. Extrapolation to zero conversion was shown to be not very efficient for the identification of primary products, since ethylene, which needs the breaking of two bonds and is a secondary product, does not disappear at zero conversion, either in their experiments or in the present work.

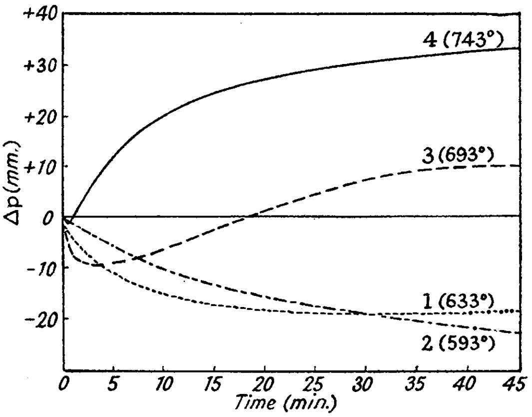
The polymer in equation (3) can subsequently decompose giving hydrogen and methane, or can combine with more *iso*butene or propylene to give higher polymers. The last column in Table 8 shows that the relation H/C in the polymer diminishes with time.

A criterion frequently used to decide upon the intervention of radicals is the use of nitric oxide, which is an inhibitor of chain reactions. In the case of *iso*butene, added nitric oxide has no effect either on the Δp–time curve or on the decomposition products. This is, however, to be expected since other olefins like propylene are inhibitors of chain reactions and it has been shown that *iso*butene is an inhibitor of the decomposition of pentane. Thus there is still the uncertainty of the primary breaking of the molecule of *iso*butene. Eltenton (*J. Chem. Phys.*, 1942, **10**, 403; 1947, **15**, 465), using a mass spectrometer, concluded that propylene reacts more easily than nitric oxide with methyl radicals, and that at high temperatures methyl and allyl radicals can be detected in the decomposition of propylene. In mechanism (1) all steps are chain-ending and so the effect of nitric oxide would be very limited.

Ethylene.—The pyrolysis of ethylene differs from that of the higher olefins in many respects and for this reason the following brief study is recorded separately. Many papers have been published on the thermal decomposition of ethylene including the following: Frey and Smith, *Ind. Eng. Chem.*, 1928, **20**, 948; Hurd, *ibid.*, 1934, **26**, 50; Burnham and Pease, *J. Amer. Chem. Soc.*, 1942, **64**, 1404; Pease, *ibid.*, 1930, **52**, 1158; Burk, Baldwin, and Whitacre, *Ind. Eng. Chem.*, 1937, **29**, 326; Storch, *J. Amer. Chem. Soc.*, 1934, **56**, 374; 1935, **57**, 2598; Wheeler and Wood, *ibid.*, 1930, **52**, 1823; Zanetti, Suydam, and Offner, *ibid.*, 1922, **44**, 2036; Schneider and Frolich, *Ind. Eng. Chem.*, 1931, **23**, 1405; Tropsch, Parrish, and Egloff, *ibid.*, 1936, **28**, 581.

General form of the Δp*–time curves.* The change in pressure of 200 mm. of ethylene at different temperatures is shown in Fig. 5. At the lower temperatures there is a decrease in pressure which, according to previous investigations, can be ascribed to polymerization of ethylene. At higher temperatures, the initial decrease in pressure is followed by an increase, and at about 700°, the form is as in the typical example of curve 3 in Fig. 5. On further increase of temperature, the initial decrease gradually disappears and near 800° only an increase of pressure is observed. This gradual change in the form of the Δp–time curve indicates that decomposition predominates at higher temperatures.

FIG. 5. Δp*–time curves for the pyrolysis of* 200 *mm. of ethylene at various temperatures.*



Order of reaction. The rate of polymerization (as determined by the initial slope of the Δp–time curve at lower temperature) was determined at pressures from 50 to 500 mm. at several temperatures (623°, 643°, 663°, 683°, 713°). The reaction was found to be exactly of the second order at each temperature.

The rate of decomposition [as determined by the tangent to the Δp–time curve at higher temperatures, or the tangent where Δp becomes positive for curves of type 3 (Fig. 5)] was determined at 10°-intervals from 713° to 783° with initial pressures from 50 to 500 mm. The reaction was of the first order up to 250 mm. but at higher pressures the order increased towards 2.

Activation energy. In Fig. 6 the values of log (rate) for the two processes (polymerization and decomposition) are plotted at different pressures. For the polymerization, the activation energy is independent of the pressure and the value of 34·6 kcal. determined agrees very well with that of Pease (*J. Amer. Chem. Soc.*, 1931, **53**, 613).

The activation energy for the decomposition seems to vary with pressure and the values are recorded in Table 9. The plot of activation energy against pressure is a straight line which on extrapolation to zero pressure gives a value of 75 kcal./g.-mol. Since the polymerization is of second order, it may well be that at higher pressures the observed decomposition rate is a function of the two processes and the value of 75 kcal. may be regarded as a minimum for the activation energy of decomposition.

It is observed in Fig. 6 that around 710° the plot of log (rate) against $1/T$ is no longer a straight line. It is at this temperature that the Δp–time curves are of type 3 (Fig. 5), and obviously the rates of polymerization and decomposition are nearly equal.

FIG. 6. *Plot of log (rate) against* $1/T$ *for ethylene at various pressures.*

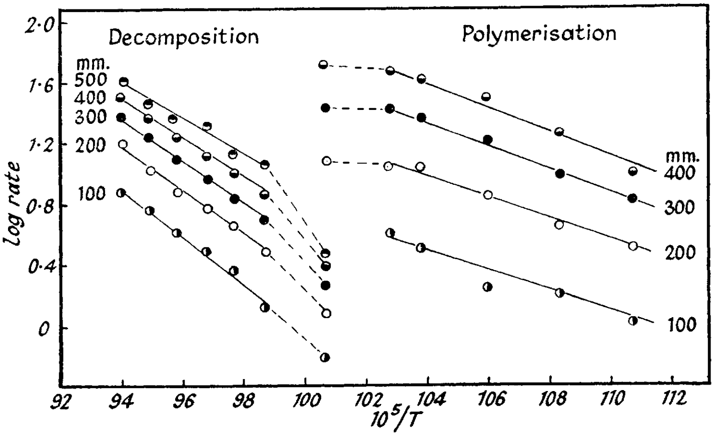
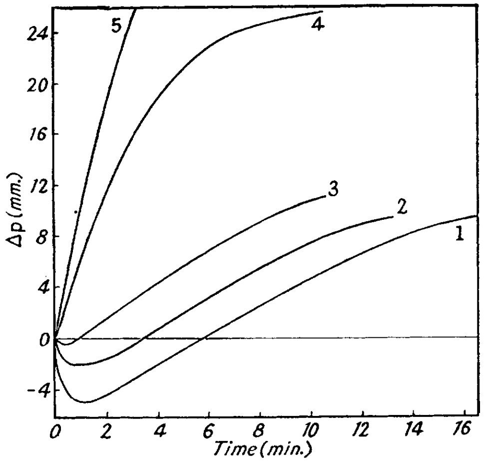


FIG. 7. ***Influence of nitric oxide on the*** Δp***–time curve for the pyrolysis of*** **200** ***mm. of ethylene at*** **713°.**



Curve 1 : *no* NO. *Curve* 2 : 50 *mm.* NO. *Curve* 3 : 13·0 *mm.* NO. *Curve* 4 : 5·0 *mm.* NO. *Curve* 5 : 96·0 *mm.* NO.

Effect of nitric oxide. Experiments carried out at 623° showed that when the Δp–time curves are of type 1 or 2 (Fig. 5), nitric oxide decreases the polymerization rate as shown in Table 10. At intermediate temperatures (713°) when the Δp–time curves are of type 1 (Fig. 7), small amounts of nitric oxide reduce the polymerization rate without affecting the decomposition (2, 3). With larger amounts of nitric oxide no decrease of pressure is observed at all, and the decomposition rate is increased (4, 5). This same accelerating effect is found at 773°.

TABLE 9. *Activation energy of ethylene decomposition.*

Press., mm. Hg	500	400	300	200	100
Act. energy, kcal./g.-mol.	57·8	62·4	64·5	68·3	70·6

TABLE 10. *Effect of nitric oxide on the rate of polymerization of ethylene.*

	Ethylene : 210 mm. Temp. : 623°					Ethylene : 200 mm. Temp. : 773°			
NO, mm. Hg	0	3·5	13·5	51·5	78·5	0	3	9	22
Rate, mm. Hg/min.	2·8	2·2	1·1	0·3	−0·15	9·8	12	14·4	30

Analytical results. Analyses were made (on a Bone and Wheeler apparatus) of the decomposition products from 200 mm. of ethylene. The results at 773° are recorded in Table 11. From the values of contraction and carbon dioxide produced in explosion the "saturated hydrocarbons plus hydrogen" appears to be exclusively methane and hydrogen.

TABLE 11. *Analysis of products from* 200 *mm. of ethylene at* 773°.*

Total press. reaction vessel	205	210	220	230	240
Δp	5	10	20	30	40
Ethylene used	123·5	131	152·15	166	170
Unsaturated	4	1	1·6	1·6	0
Satd. hydrocarbons + hydrogen	102	130	164	190	208
Contraction (after expl.)	182	234	308	333	357
CO_2 (from expl.)	65·7	83	94	98	110
CH_4	65·7	83	94	98	110
H_2	36·3	47	70	92	98

* All pressures are expressed as mm. of mercury.

The percentages of carbon and hydrogen not accounted for in the gaseous product are recorded in Table 12. The percentage of carbon accounted for remains fairly constant, but that of hydrogen decreases with time, indicating that the condensed product is losing hydrogen. The carbon/hydrogen ratio of the polymer therefore increases with time, and ultimately it would probably lose all its hydrogen, leaving only carbon. At this high temperature (773°) the products of the polymerization obviously decompose, and in fact the reaction vessel is quickly coated with a thin layer of carbon.

TABLE 12. *Percentages of carbon and hydrogen* not *accounted for in gaseous product.*

Δp, mm. Hg	5	10	20	30	40
% C not accounted for	73	68	68	74	67
% H not accounted for	32	18	15	13	6
C/H in condensed product	1·1	1·8	2·2	2·6	5·2

Analyses were also made at 733°, 693°, and 623°. At each temperature the amount of carbon dioxide produced in the explosion showed that in addition to methane higher paraffins are produced.

At the lower temperature (623°) the ethylene is consumed according to a second-order equation, but gaseous products (paraffins + hydrogen) are found in the decomposition products, 30% of the carbon atoms being accounted for in the gaseous phase.

Conclusion.—The major question which arises from the foregoing experimental results for ethylene is whether the polymerization and decomposition are simultaneous processes or whether polymerization occurs first and is followed by the decomposition of the polymer formed.

The following facts are in favour of consecutive processes : At the lower temperatures (623°) the ethylene is used up according to a second-order equation, but gaseous products (paraffins plus hydrogen) are found in the decomposition products, 30% of the carbon atoms being accounted for in the gaseous phase. The activation energy for decomposition varies with pressure, giving an extrapolated value of 75 kcal./mol. at zero pressure. There is a production of both polymer and gaseous products at all temperatures studied, and it has been proved that the polymer decomposes at 773° becoming poorer in hydrogen.

The effect of nitric oxide is more suggestive of simultaneous processes. Its inhibitory effect on the polymerization probably means that it reacts with radicals and thereby breaks chains. If under the action of nitric oxide no polymer is formed, none could decompose, so that the decomposition process would automatically be inhibited. This does not happen and thus simultaneous processes are indicated. This conclusion is however, rendered somewhat uncertain in so far as the acceleration produced by nitric oxide might be due to an actual oxidation of ethylene.

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