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This is the familiar equation for the osmotic pressure of a high polymer solution except for the substitution of $\bar{m}_n$ for m and μ^* for μ. We may transform from volume fractions to concentrations (grams per cc) by noting that $c=\phi\rho$ where ρ is the density in grams per cc. We then obtain:

$$\pi=RT[(c_p/\bar{M}_n)+(\tfrac{1}{2}-\mu^*/V_0\bar{\rho}^2)c_p{}^2+\cdots], \quad (29)$$

where $\bar{M}_n$ is the number average molecular weight, defined as

$$(c_p/\bar{M}_n)=(c_1+c_2/\bar{M}_n)=(c_1/M_1)+(c_2/M_2), \quad (30)$$

and $\bar{\rho}$ is the harmonic mean of the densities if expressed as a function of concentration, or the arithmetic mean taken as volume fractions:

$$\bar{\rho}=c_1+c_2/(c_1/\rho_1)+(c_2/\rho_2)=\phi_1\rho_1+\phi_2\rho_2/\phi_1+\phi_2$$
$$=\theta_1\rho_1+\theta_2\rho_2. \quad (31)$$

By the usual technique of plotting π/c against c, we may use the slope of the line to determine the coefficient of c^2 and, hence, μ^*. Since μ_{10} and μ_{20} are known, we can use the variation of μ^* with θ (Eq. (27)) to determine μ_{12}, which cannot be determined directly.

ACKNOWLEDGMENTS

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The Kinetics of the Thermal Decomposition of Propylene

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The thermal decomposition of propylene was investigated for temperatures ranging from 680°C up to 870°C and with percentages of decomposition from 0.01 percent up to about 2 percent. The reaction was shown to be a homogenous gas reaction of the first order, the first-order constant being given by an expression $1.1\cdot10^{13}\exp-(72{,}000/RT)$. Two mechanisms are discussed, both of which account for the observed kinetics and products of decomposition. It is demonstrated that the first step in the thermal decomposition of propylene is the splitting of the C—H bond leading to the formation of H atoms and allyl radicals. The problem of the value of D(C—H) in propylene is discussed in the light of the two suggested mechanisms. An attempt is made to account for the variety of the reactions between H atoms and propylene molecules as observed by various investigators.

ALTHOUGH several investigations of the pyrolysis of propylene have been carried out within the last twenty years, we still lack a full understanding of the mechanism of this process. In particular, the first steps of this decomposition are not definitely known, and the present research was an attempt to clarify this problem. We shall start with a brief summary of the results obtained by previous investigations, confining our discussion to those processes which are homogenous gas reactions.*

Frey and Smith[1] studied the decomposition of propylene in a silica vessel at 575°C and atmospheric pressure, using a flow method and a time of contact of 1–4 minutes. They found that this process was a homogenous gas reaction. Analysis of the gases showed CH_4 and C_2H_4 to be the main products of the decomposition, in addition to smaller quantities of H_2, C_2H_6, and higher hydrocarbons. Assuming that the C_2H_6 resulted from the hydrogenation of a part of the originally formed C_2H_4, we find from the data of these authors that the CH_4/C_2H_4 ratio is 1:1 ($CH_4=10.7$ percent, $C_2H_4=8.0$ percent, and $C_2H_6=1.9$ percent). This is the ratio which we might expect on the basis of the mechanism suggested later in the discussion of our results. Assuming also that the hydrogenation of C_2H_4 to C_2H_6 and C_3H_6 to C_3H_8** consumed a part of the H_2 originally formed, we find the CH_4/total H_2 ratio as 2:1. This is the CH_4/H_2 ratio found in the present research.

Kinetic studies of the thermal decomposition of propylene were provided by Hurd and Meinert,[2] who investigated this reaction between 600°C and 700°C under atmospheric pressure in a flow system.

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* A review of the earlier literature is given by G. Egloff and E. Wilson, Ind. Eng. Chem. **27**, 917 (1935).

[1] F. E. Frey and D. F. Smith, Ind. Eng. Chem. **20**, 948 (1928).

** Frey and Smith found, indeed, that under their experimental conditions the hydrogenation of C_2H_4 and C_3H_6 by H_2 occurs easily.

[2] C. D. Hurd and R. N. Meinert, J. Am. Chem. Soc. **52**, 4978 (1930).

They stated that the decomposition in a silica or Pyrex vessel was a homogenous, first-order gas reaction (proved by packing the reaction vessel and by diluting the propylene with nitrogen). They reported CH_4, C_2H_4, and H_2 to be the main products of the pyrolysis. The composition of the gases was changed only slightly by varying the temperature or time of contact. The CH_4/C_2H_4 ratio was 1:1 in agreement with the above-mentioned interpretation of Frey and Smith's results. In addition to gaseous products, they isolated liquid products of an aromatic character, resulting probably from the polymerization favored by the high pressure of propylene (the dilution of propylene by N_2 decreased the amount of these liquid products). Neither allene, nor products of its polymerization, were found in the pyrolyzed material. This point, which is in a sharp contradiction to our present finding, deserves special consideration, and we shall return to it later in the discussion.

The third work which should be mentioned is that of Tropsch, Parrish, and Egloff.[3] These authors used an extremely short time of contact (about 0.001 sec.), but unfortunately they chose such a high temperature of pyrolysis (1100°C–1400°C), that all the propylene was decomposed. Therefore, it is impossible to draw any conclusion about the mechanism of decomposition from their data.

EXPERIMENTAL

Apparatus and Technique

The apparatus and the technique were essentially the same as used previously for the pyrolytical studies of toluene and the xylenes.[4] The propylene was kept in a 25-l storage flask, and was introduced into a silica reaction vessel through a needle valve and a capillary. Adjustment of the needle valve made it possible to vary the pressure of propylene in the reaction vessel. The quantity of propylene passed into the reaction vessel was measured by the pressure drop in the storage flask. The pyrolyzed gas passed through a *U*-shaped trap, cooled to −80°C, and then through a large trap cooled by liquid air. Here all the undecomposed propylene was frozen out (as well as any other products of the decomposition, except CH_4 and H_2). The H_2 and CH_4 formed during the pyrolysis were continuously pumped out by a system of two mercury pumps into 1.5-l storage vessel as described in the previous communication.[4]

The extent of the pyrolysis was measured by the quantity of H_2 and CH_4 formed, it being assumed that each mole of H_2 or CH_4 corresponds to one mole of propylene decomposed originally. After the conclusion of a series of experiments the recovered propylene could be distilled in vacuum into a trap, from which it could be returned to the 25-l storage flask. In such a way the pyrolyzed material could be re-used. This arrangement made it possible to investigate the propylene previously pyrolyzed any required number of times.

TABLE I.

Run		Pretreatment of propylene. No. of previous pyrolyses	T°C	P·mm Hg	Time of contact: sec.	$K\cdot 10^3$ sec.$^{-1}$	
							$K_{780}\cdot 10^3$ sec.$^{-1}$*
4	First batch of propylene	Once at 780°C	778	8.4	0.149	14.5	15.7
5		Once at 780°C	778	8.3	0.148	15.0	16.2
6		Once at 780°C	781	8.3	0.151	16.6	16.0
7		Twice at 780°C	781	8.3	0.147	15.1	14.5
8		Twice at 780°C	780	8.3	0.147	14.5	14.5
9		Twice at 780°C	780	8.2	0.144	14.8	14.8
11		3 times at 780°C	780	8.3	0.144	15.8	15.8
59		Once at 830°C	781	8.9	0.127	14.9	14.3
60		Once at 830°C	781	8.7	0.143	16.3	15.7
71	Second batch of propylene	Once at 780°C	781	8.7	0.150	14.8	14.3
75		Twice at 780°C	785	8.9	0.148	18.1	14.1
							$K_{746}\cdot 10^3$ sec.$^{-1}$*
18	First batch of propylene	4 times at 770°C	745	6.6	0.119	4.8	5.1
19		4 times at 770°C	747	8.1	0.152	5.7	5.5
21		5 times at 770°C	746	8.6	0.155	5.4	5.4
22		5 times at 770°C	745	8.5	0.153	5.0	5.2
23		5 times at 770°C	746	8.0	0.108	5.0	5.0
61		Once at 830°C	748	8.9	0.154	5.7	5.3
93	Second batch	Once at 800°C	746	8.7	0.146	5.3	5.3

* This column gives the *k* interpolated to a constant temperature for the sake of comparison.

The Material Used for Pyrolysis

The propylene used in this study was generously supplied by Petrochemicals, Ltd., Manchester. Two samples from different batches were investigated in order to ascertain the reproducibility of the results and their independence of incidental impurities. The analysis of the gas showed that both batches contained over 99.3 percent of propylene. The propylene was further purified by vacuum distillation from −80°C into a trap cooled by liquid air and connected to a high vacuum pump. The condensed gas was evacuated for a couple of hours, before it was ultimately led into the 25-l storage flask.

In spite of these precautions it was found that the unpyrolyzed propylene decomposed at a rate slightly lower than that which had been pyrolyzed. However, one pyrolysis at a temperature not lower than 770°C yields a product which in any subsequent pyrolysis decomposed at a constant rate. This point was carefully examined. Table I demonstrates

TABLE II.

	Run	T°C	P·mm Hg	$K\cdot 10^3$ sec.$^{-1}$	Percent H_2	Percent CH_4
Not packed	50	810	8.3	46	28	72
Packed	105	813	8.4	57	—	—
Packed	106	808	8.4	45	30	70

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[3] H. Tropsch, C. I. Parrish, and G. Egloff, Ind. Eng. Chem. 28, 581 (1936).

[4] M. Szwarc, J. Chem. Phys. 16, 128 (1948).

TABLE III.

	Run	T°C	P·mm of Hg	Time of contact sec.	Percent of decomp.	$K\cdot10^3$ sec.$^{-1}$	
			T round 717°C				$K_{717}\cdot10^3$ sec.$^{-1}$
	67	718	3.1	0.182	0.038	2.1	2.0
	64	714	3.6	0.152	0.027	1.8	2.0
	65	717	8.5	0.155	0.033	2.1	2.1
	66	718	14.6	0.120	0.028	2.4	2.3
			T round 746°C				$K_{746}\cdot10^3$ sec.$^{-1}$
	63	746	4.5	0.180	0.102	5.6	5.6
	61	746	8.9	0.154	0.088	5.7	5.7
	62	746	13.6	0.137	0.079	5.8	5.8
			T round 780°C				$K_{780}\cdot10^3$ sec.$^{-1}$
	12	780	2.2	0.150	0.22	14.9	14.9
	13	780	4.2	0.118	0.19	15.7	15.7
	9	780	8.2	0.144	0.21	14.8	14.8
	11	780	8.3	0.144	0.23	15.8	15.8
	10	782	14.4	0.124	0.25	19.9	18.3
Longer time of contact	17	778	2.7	0.602	0.76	12.5	13.5
	15	780	6.3	0.580	0.86	14.8	14.8
	14	780	11.3	0.448	0.88	19.7	19.7

clearly that the rate of decomposition was independent of the number of previous pyrolyses and it did not depend on the temperature at which the previous pyrolyses had been performed (provided that at least one of the previous pyrolyses had been carried out at a temperature ⩾770°C). This constant rate was taken as the true rate of decomposition of propylene.

The inspection of the data presented in Table I proves that both batches of propylene decomposed at the same rate. It should be noted also that the reproducibility of the results was extremely good (the deviations from the average value were less than 10 percent).

The Kinetics of the Decomposition

The decomposition of propylene was shown to be a homogenous gas reaction of the first order. The homogenity was demonstrated by packing the reaction vessel with silica wool which increased the surface by factor of 6. The data for the packed and empty reaction vessel are given in Table II.

The first order of the reaction was demonstrated by varying the pressure of propylene by factor of 7 (from 2 mm of Hg up to 14 mm of Hg), and by varying the time of contact by factor of 6 (from 0.1 sec. up to 0.6 sec.). Table III contains the results obtained for various pressures of propylene and various times of contact.

The unimolecular k seems to be fairly constant, although a closer examination of the data reveals a trend with increasing pressure of propylene. This trend is most noticeable with longer times of contact (runs No. 17, 15, 14) amounting to about a 40 percent increase in k for a fourfold increase in the pressure of propylene.

The variation of the unimolecular k with temperature is recorded in Table IV, and the plot of log k against $1/T$ is given in Fig. 1. Each point in this graph represents the average of at least five experiments. It should be noted that the Arrhenius law is obeyed over the whole investigated range of temperatures from 680°C up to 870°C (i.e., over 190°C). Figure 1 enables us to estimate the energy of activation at 72.0±3.0 kcal./mole and the frequency factor at $1.1\cdot10^{13}$.

The Products of Decomposition

The pyrolysis of propylene produced CH_4 and H_2 in a nearly constant proportion of about 2:1. Table V contains the results of analysis of the

TABLE IV.

Run	T°C	P·mm Hg	Time of contact sec.	Percent of decomp.	$K\cdot10^3$ sec.$^{-1}$	
35	686	8.7	0.185	0.0067	0.36	
36	686	8.7	0.180	0.0063	0.35	Average for
37	685	8.6	0.185	0.0063	0.34	685°C
38	683	8.3	0.187	0.0056	0.30	$0.34\cdot10^{-3}$
39	685	8.7	0.192	0.0064	0.32	
29	698	8.7	0.210	0.021	0.99	
30	698	8.7	0.167	0.015	0.92	Average for
31	699	8.6	0.165	0.017	1.03	698°C
32	698	8.4	0.159	0.015	0.94	$0.95\cdot10^{-3}$
33	698	8.5	0.143	0.013	0.94	
24	723	8.5	0.157	0.033	2.12	
25	723	8.3	0.155	0.032	2.09	Average for
26	724	8.7	0.170	0.038	2.24	723°C
27	725	8.6	0.160	0.039	2.44	$2.12\cdot10^{-3}$
28	723	8.5	0.165	0.032	1.94	
18	745	6.6	0.119	0.058	4.9	
19	747	8.1	0.152	0.087	5.7	Average for
21	746	8.6	0.155	0.083	5.4	745°C
22	745	8.5	0.153	0.077	5.0	$5.05\cdot10^{-3}$
23	746	8.0	0.108	0.054	5.0	
4	778	8.4	0.149	0.22	14.5	
5	778	8.3	0.148	0.22	15.0	Average for
6	781	8.3	0.151	0.25	16.6	780°C
7	781	8.3	0.147	0.22	15.1	$15.5\cdot10^{-3}$
8	780	8.3	0.147	0.21	14.5	
9	780	8.2	0.144	0.21	14.8	
50	810	8.3	0.138	0.64	46	
51	811	8.1	0.135	0.65	48	Average for
52	810	8.4	0.139	0.66	47	810°C
53	811	8.5	0.135	0.58	43	$44.6\cdot10^{-3}$
54	811	8.4	0.132	0.59	45	
55	811	8.5	0.145	0.64	44	
44	857	8.4	0.149	1.95	131	
45	857	8.4	0.130	1.70	131	Average for
46	859	8.4	0.155	2.18	141	857°C
47	858	8.6	0.117	1.53	131	$128\cdot10^{-3}$
48	857	8.7	0.138	1.72	124	
56	872	9.2	0.138	3.54	256	

TABLE V.

Run	T°C	P·mm Hg	Per-cent H_2	Per-cent CH_4	Previous treatment
64	704	8.6	22	78	Once pyrolyzed at 830°C
65	707	8.5	26	74	Once pyrolyzed at 830°C
61	746	8.9	29	71	Once pyrolyzed at 830°C
10	782	14.4	28	72	3 times pyrolyzed at 780°C
75	785	8.9	30	70	2 times pyrolyzed at 780°C } Second
74	791	3.1	30	70	Once pyrolyzed at 780°C } batch
79	791	14.0	32	68	Once pyrolyzed at 780°C
50	810	8.3	28	72	2 times pyrolyzed at 850°C
54	811	8.4	28	72	3 times pyrolyzed at 850°C
57	830	8.6	32	68	Once pyrolyzed at 830°C
40	851	8.1	30	70	Not pyrolyzed
44	851	8.4	32	68	Once pyrolyzed at 850°C
69	868	9.1	32	68	3 times pyrolyzed at 870°C
56	872	9.1	32	68	3 times pyrolyzed at 850°C

CH_4+H_2 mixture. It should be noted that the ratio of CH_4/H_2 does not depend on the pressure of propylene, and is not influenced by the previous pyrolysis of the investigated sample of propylene. A very slight decrease in the CH_4/H_2 ratio was observed with increasing temperatures. The analysis of the gas formed in the decomposition at 710°C gave 74–78 percent of CH_4, whereas at 870°C the percentage of CH_4 in the gas dropped to 68–70 percent. On the assumption that the change of CH_4/H_2 ratio with temperature depends on the difference in the energies of activation of the processes leading to the formation of CH_4 and H_2, respectively, we conclude that

$$E_{\text{act.H}_2}-E_{\text{act.CH}_4}=2-4\ \text{kcal./mole.}$$

In order to get simple kinetics and to avoid all reactions due to the accumulation of products, we limited the percentage of decomposition to 0.01 percent–2 percent. The investigation of the products of decomposition other than H_2 and CH_4 was therefore feasible only for runs made at higher temperatures, and even in these cases the results were of a qualitative, rather than quantitative, nature. The other products of decomposition were found to be C_2H_4 and allene by fractional distillation on the Podbielniak type still of propylene pyrolyzed two or three times at 850°C–870°C. The allene fraction was identified by its boiling point (−33°C–−35°C) and by the reaction obtained with solution of $HgCl_2$ (white precipitate). The quantities suggested that one mole of C_2H_4 was produced for every mole of CH_4, and one mole of allene was produced for each mole of CH_4 or H_2.

Very small quantities of yellowish liquid were observed in propylene pyrolyzed repeatedly at highest temperature. The boiling point of this liquid was about 60°C, suggesting it was C_6 hydrocarbon. Its quantity was 10–15 mole percent of H_2+CH_4 (calculating it as C_6 hydrocarbon). No non-volatile or polymeric substances were observed.

In a further attempt to identify the products of reaction (other than H_2 and CH_4), the whole pyrolyzed propylene was brominated. The bromination product was carefully fractionated, and the high boiling fraction was collected separately. The typical analysis of this fraction was

	C	H	Br
High boiling fraction	11.4%	1.4%	87.1%
Theoretical $CH_2Br\cdot CBr_2\cdot CH_2Br$	10.0%	1.1%	88.9%
Theoretical $CH_2Br\cdot CHBr\cdot CH_2\cdot CH_2\cdot CHBr\cdot CH_2Br$	17.9%	2.5%	79.6%

This shows that the high boiling fraction consisted mainly of tetrabromallene with perhaps small quantities of tetrabromdiallyl. The quantities of these high boiling fractions indicated again the 1:1 ratio of (H_2+CH_4)/allene.

Influence of Addition of Diallyl and Allene

As our experimental technique is extremely sensitive to small amounts of impurities, it was desirable to find how the addition of diallyl and allene influences the rate of decomposition of propylene. It was demonstrated that addition of very small quantities of diallyl was without any effect (up to few tenths of percent). However, greater quantities (1 percent–4 percent) of diallyl increased considerably the rate of decomposition of propylene. The addition of 4 percent of diallyl also changed the composition of the H_2+CH_4 mixture. After this

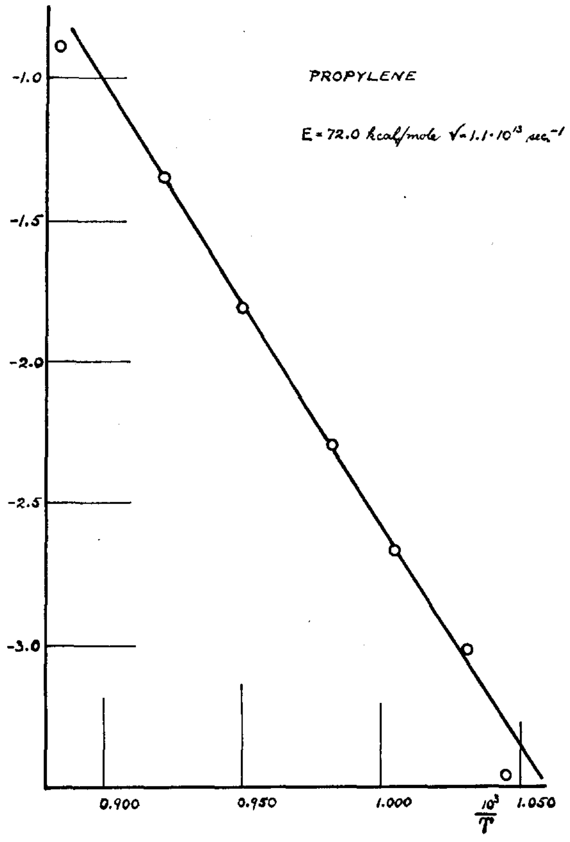

FIG. 1.

addition the rate of decomposition increased by a factor of 3, while the percent of H_2 increased from about 30 percent (observed for the pure propylene) to nearly 50 percent. The results of these experiments are given in Table VI.

We conclude from these results that diallyl is not the main product of decomposition of propylene, since samples of pyrolyzed propylene which contained about 6 percent of decomposition products still gave the same rate of decomposition on subsequent pyrolysis. Addition of allene (up to 8 percent) caused no appreciable change in the rate of decomposition of propylene.

DISCUSSION

Two distinct mechanisms of the decomposition of propylene can account for the observed facts. We shall start by formulating both mechanisms, then indicate how they account for the experimental data, and finally discuss how it is possible to decide which is the correct one.

Mechanism 1

$$CH_2{=}CH-CH_3\rightarrow CH_2{=}CH-CH_2\cdot+H; \qquad (1)$$

$$CH_2{=}CH-CH_3+H\rightarrow CH_2{=}CH-CH_2\cdot+H_2; \qquad (2)$$

$$\left\{\begin{array}{ll} CH_2{=}CH-CH_3+H\rightarrow C_2H_4+CH_3\cdot; & (3a) \\ CH_2{=}CH-CH_3+CH_3\cdot\rightarrow CH_2{=}CH-CH_2\cdot+CH_4; & (3b) \end{array}\right.$$

$$2CH_2{=}CH-CH_2\cdot\rightarrow CH_2{=}CH-CH_3+CH_2{=}C{=}CH_2. \qquad (4)$$

Mechanism 2

$$CH_2{=}CH-CH_3\rightarrow CH_2{=}CH-CH_2\cdot+H; \qquad (1)$$

$$CH_2{=}CH-CH_2\cdot\rightarrow CH_2{=}C{=}CH_2+H; \qquad (5)$$

$$CH_2{=}CH-CH_3+H\rightarrow CH_2{=}CH-CH_2\cdot+H_2; \qquad (2)$$

$$\left\{\begin{array}{ll} CH_2{=}CH-CH_3+H\rightarrow C_2H_4+CH_3\cdot; & (3a) \\ CH_2{=}CH-CH_3+CH_3\cdot\rightarrow CH_2{=}CH-CH_2\cdot+CH_4; & (3b) \end{array}\right.$$

$$CH_2{=}CH-CH_2\cdot+H\rightarrow CH_2{=}CH-CH_3. \qquad (6)$$

TABLE VI.

Run	T°C	Percent diallyl.	$K\cdot 10^3\cdot$sec.$^{-1}$
82	810	0.00	45.1
83	811	0.05	43.7
84	812	0.2	45.3
85	812	0.2	45.5
86	812	1.0	85.0
87	812	1.0	75.0
89	812	4.0	140
90	812	4.0	142

Mechanism 1

This mechanism is essentially the one which was previously proposed to account for the decomposition of toluene, the xylenes,[4, 5] the fluorotoluenes,[6] and the picolines.[7] Reaction 1 is the rate determining step which is followed by the rapid reactions (2), (3a), and (3b). The reactions (2) and (3a) represent the two ways in which the H atoms are removed from the system. The first leads to the formation of H_2, the second to that of CH_4 and C_2H_4. It is obvious from an inspection of reactions (3a) and (3b) that this mechanism requires the CH_4/C_2H_4 ratio to be 1:1. This ratio was deduced previously from the data of Frey and Smith,[1] and it was explicitly reported by Hurd and Meinert.[2] Our present experiments seem to confirm this 1:1 ratio, although no exact determination was possible owing to the extremely low percentages of decomposition at which we worked.

Since H_2 and CH_4 are alternative products of the same reaction

$$CH_2{=}CH-CH_3+H \begin{array}{l} \nearrow CH_2{=}CH-CH_2\cdot+H_2 \\ \searrow C_2H_4+CH_3\cdot, \end{array}$$

the CH_4/H_2 ratio should be independent of the pressure of propylene. This was confirmed in runs 10, 75, 74, and 79. (See Table V.) The energies of activation for both reaction paths are certainly small, and therefore the CH_4/H_2 ratio which is dependent on their difference should be nearly independent of temperature (see Table V).

A further conclusion which can be drawn from the proposed mechanism is that the (H_2+CH_4)/allene ratio should be 1:1. Our data seem to confirm this conclusion. Allene was definitely found as one of the products of decomposition. Taking into account some losses caused by the polymerization of allene to the observed C^6 hydrocarbon, we find a fair agreement between the actually estimated quantity of allene and that calculated (equal to H_2+CH_4). For example, the calculated quantity of allene was 8 percent while the observed was 5 percent. Hurd and Meinert reported that the pyrolysis of allene[8] gave some liquid polymer as a main product of reaction, but they found, as previously noted, neither allene nor the above-mentioned liquid products in the pyrolysis of propylene.[2] The following explanation is suggested in order to reconcile these results with ours. Allene was indeed formed in the experiments

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[5] M. Szwarc, Nature **160**, 403 (1947).

[6] M. Szwarc and J. S. Roberts, J. Chem. Phys. **16**, 609 (1948).

[7] J. S. Roberts and M. Szwarc, J. Chem. Phys. **16**, 981 (1948).

[8] R. N. Meinert and C. D. Hurd, J. Am. Chem. Soc. **52**, 4540 (1930).

of Hurd and Meinert, but it co-polymerized with propylene. Therefore, the resulting liquid products, which were found by Hurd and Meinert in pyrolysis of propylene, differed from the products of polymerization of pure allene.

Kinetically, mechanism 1 represents a true unimolecular reaction. Hence it accounts for the first-order decomposition and the 10^{13} frequency factor, which is theoretically required for true unimolecular reactions.[9]

Mechanism 2

This mechanism is a chain process in which reaction (1) is the chain initiation, reactions (5) and (2) or (5), (3a), and (3b) are alternative chain propagation, and, finally, reaction (6) is the chain termination.***

Inspection of the suggested reaction scheme shows that mechanism 2 also requires the ratio CH_4/C_2H_4 to be 1:1, the ratio CH_4/H_2 to be independent of pressure of propylene and only slightly dependent on temperature, and, finally, the (CH_4+H_2)/allene ratio to be 1:1 (on the same grounds as given before in the discussion of mechanism 1).

Using the stationary state method we obtain the following expression for the rate of reaction:

$$d(\text{gas})/dt=(k_1\cdot k_5\cdot k_2/k_6)^{\frac{1}{2}}\cdot(\text{propylene}).$$

For the sake of simplicity we considered in this expression only reactions (5) and (2) as the chain propagation, but the final result is not changed if we consider the alternative chain propagation, namely, reactions (5), (3a), and (3b).

Reactions (1) and (5) are unimolecular decompositions of the propylene and allyl radicals, respectively. Both, therefore, should have frequency factor of the order 10^{13}. The energy of activation of (1) is equal to $D(C-H)$ in propylene, that of (2) is equal or slightly greater than $D(C-H)$ in the allyl radical. The sum of $D(C-H)$ in propylene and $D(C-H)$ in the allyl radical is given by thermochemical data as the endothermicity of the following reaction:

$$CH_3-CH=CH_2\rightarrow CH_2=C=CH_2+2H-145\ \text{kcal}.$$

We see, therefore, that $(k_1\cdot k_5)^{\frac{1}{2}}\sim 10^{13}\cdot\exp(72.5/RT)$. Now, k_2 and k_6 are the rate constants for the bimolecular reactions $H+CH_3-CH=CH_2$ and $H+\cdot CH_2-CH=CH_2$, respectively. We should expect that both constants correspond to the same collision factor. Also, since the energy of activation of (2) is very small and that of (6) probably zero, we can assume in the first approximation $k_2\sim k_6$.

We came to the conclusion that the mechanism 2 gives first-order kinetics, with a frequency factor of the order 10^{13} and an energy of activation about 72 kcal./mole. Thus, mechanism 2 accounts for all observed features of the decomposition of propylene.

THE DISTINCTION BETWEEN MECHANISM 1 AND MECHANISM 2

As was shown in the previous paragraphs, both mechanisms require the same products of reaction, in the same proportions, the same order of decomposition with the same frequency factor and energy of activation. To distinguish between them we must use indirect methods. The most elegant way would be provided by a study of the decomposition of either or both deuterium compounds *A* and *B*.

$$\underset{A}{CH_2=CH-CD_3};\quad \underset{B}{CH_2=CD-CH_3}.$$

According to mechanism 1, *A* should give pure D_2, while *B* should give pure H_2. According to mechanism 2, both compounds should give a mixture of deuterium and hydrogen, and the amount of hydrogen in deuterium in case of *A*, or deuterium in hydrogen in case of *B*, would provide a measure of the length of the chain. Unfortunately, we are unable to obtain these compounds at present and therefore we must abandon this approach for the time being.

We turn, therefore, to the conclusions which can be drawn from the reported experimental facts, on the basis of the suggested mechanisms. Mechanism 1 demands that the observed energy of activation of 72 kcal./mole should be equal to the $D(C-H)$ in propylene (assuming as usual that the energy of activation for recombination of H atoms and radicals is zero). This is a surprisingly low value, although not quite impossible. There are good reasons to believe that the $D(C-H)$ in propylene is lower than $D(C-H)$ in toluene. Taylor and Smith[10] found that CH_3 radicals extract H atoms more easily from propylene than from toluene; Butler and Polanyi[11] found the rate of decomposition of allyl iodide to be greater than that of benzyl iodide and the same observation was made by Shaw and the present author[12] using a static method. The $D(C-H)$ in toluene was estimated at 77.5 kcal/mole.[4] It should be emphasized that in the case of toluene and its derivatives there is no ambiguity of interpretation such as is found in the case of propylene.

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[9] M. Polanyi and E. Wigner, Zeits. f. physik. Chemie **A139**, 439 (1928).

*** The other chain terminations, i.e., $H+H+M\rightarrow H_2+M$, or $2CH_2=CH-CH_2\cdot\rightarrow CH_2=C=CH_2+CH_3\cdot CH=CH_2$ have been ruled out on the energetical basis. The former requires $Ea\sim\frac{1}{2}D(C-H)$, i.e., $D(C-H)$ in propylene would be ~ 144 kcal./mole. The latter gives $Ea\sim 145-\frac{1}{2}D(C-H)+X$ leading to $D(C-H)$ in propylene $\geqslant 146$ kcal./mole. Both values are, of course, impossible.

[10] H. S. Taylor and J. O. Smith, J. Chem. Phys. **8**, 543 (1940).

[11] E. T. Butler and M. Polanyi, Trans. Faraday Soc. **39**, 19 (1943).

[12] A. Shaw and M. Szwarc, unpublished results.

However, on the basis of present thermochemical data, the value of 72 kcal./mole as $D(C-H)$ in propylene leads to the value of 30 kcal./mole for the heat of dissociation of the central $C-C$ bond in diallyl.[****] This value is hardly acceptable, and it seems to be too low. To get more information on this subject some crude experiments of pyrolysis of diallyl were performed. No effect was observed on heating diallyl vapor at pressure of 60 mm of Hg and 180°C over a period of 16 hours. There was no increase of pressure, and the vapor could be condensed at -80°C, leaving no non-condensable residue. The pressure observed in this experiment was equal to the calculated value on the basis of the ideal gas law, i.e., there was no appreciable dissociation of diallyl into allyl radicals.

Heating at about 350°C caused some reaction with production of gas, which was not condensable in liquid air (probably H_2). The matter was not pursued further.

In conclusion we can say that this low value for the $D(C-C)$ in diallyl is the important argument against mechanism 1 and at present perhaps the only one.

Turning now to mechanism 2, we can suppose that the chain is probably a very short one. The argument is taken from our study of pyrolysis of isobutene (the following paper), which seems to be a chain process, similar to that outlined in the present paper. In the case of isobutene the maximum chain length is given by the CH_4/H_2 ratio which was found to be about 9. It is plausible to assume that the length of the chain in the decomposition of propylene should be no longer, as the removal of H atom from allyl radical probably requires 12 kcal. more than the removal of CH_3 group from the similar methyl-allyl radical.[†]

Another argument in favor of a short chain is provided by our experiments with a propylene-diallyl mixture. Diallyl should dissociate into allyl radicals, and if these radicals decompose as demanded by mechanism 2, the rate of reaction should increase very considerably. In fact, the addition of 0.2 percent of diallyl (which is comparable with the percent of decomposition of pure propylene at the temperature of this experiment) caused no appreciable change in the rate of decomposition. This result can be even regarded as an argument against mechanism 2.

If we assume that the chain is short, say about 10, we are able to calculate the difference in energies of activation of processes 1 and 5 from the following expression,

$$E_1-E_5=2.\,RT[\ln.\,(\text{chain length})+\tfrac{1}{2}\ln\cdot 3]$$

which is the straightforward conclusion from mechanism 2. The term $\frac{1}{2}\ln\cdot 3$ comes as a result of three times greater frequency factor for k_1 than for k_5 (on statistical grounds). Thus we find

$$E_1-E_5\sim 11 \text{ kcal./mole,}$$
$$E_1+E_5\sim 145 \text{ kcal./mole}$$
(from thermochemical data),

and in result $E_1\sim 78$ kcal./mole. This value corresponds to the frequency factor $2.5\cdot 10^{13}$ for the unimolecular constant corresponding to the first step in the decomposition of propylene, in good agreement with the frequency factors found for toluene and the xylenes,[4] and leads to much more plausible value of 42 kcal./mole for the $D(C-C)$ of the central $C-C$ bond in diallyl. It should be noticed, however, that this calculation of $D(C-H)$ in propylene was based on the approximation $k_2\sim k_6$.

The Reactions between Hydrogen Atoms and Propylene

Both suggested mechanisms of decomposition of propylene assume two reactions between H atoms and C_3H_6, namely,

$$H+CH_3\cdot CH=CH_2\rightarrow H_2+\cdot CH_2-CH=CH_2, \quad (2)$$

$$H+CH_3\cdot CH=CH_2\rightarrow CH_3\cdot +C_2H_4. \quad (3)$$

The variation of CH_4/H_2 ratio with temperature indicates that the energy of activation of (2) is by 2–4 kcal. greater than that of (3). The reaction (3) most probably goes in two steps:

$$H+CH_3-CH=CH_2\rightarrow CH_3-CH_2-CH_2, \quad (A)$$

$$CH_3-CH_2-CH_2\rightarrow CH_3+C_2H_4. \quad (B)$$

The "hot" radical formed in step (A) decomposes easily into CH_3 radical and C_2H_4, as the over-all process is exothermic to an extent of 13 kcal. The attack of H atom on the other end of the double bond seems to be ineffective. The "hot" radical $CH_3\cdot CH\cdot CH_3$ formed by such a process should decompose into its original components, i.e., propylene and an H atom. The decomposition into CH_3 and $CH_3\cdot CH$ seems to be energetically improbable (very likely an endothermic process).

It should be noted that a change of the conditions under which H atoms interact with propylene changes profoundly the ultimate products of reaction. The extraction of H atoms and formation of

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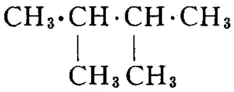
[****] The heat of formation of gaseous diallyl can be obtained from the heat of combustion of liquid diallyl (Coops, Mulder, Dienske, and Smittenberg, Rec. Trav. Chim. **65**, 128 (1946), taking 8 kcal./mole for the heat of vaporization, or from Rossini's heat of formation of *n*-hexane in conjunction with Kistiakowsky's heat of hydrogenation of diallyl. Both methods give the same value.

[†] While the endothermicity of the reaction $CH_3-CH=CH_2\rightarrow CH_2=C=CH_2+2H$ is 145 kcal., the endothermicity of the reaction $(CH_3)_2{:}C=CH_2\rightarrow CH_2=C=CH_2+H+CH_3$ is 133 kcal. Since the $D(C-H)$'s in propylene and isobutene are probably very similar, the difference of 12 kcal. should be mainly accounted for by the difference between removal of H from allyl radical and CH_3 from the methyl-allyl radical.

allyl radicals seem to be suppressed very considerably at normal or slightly elevated temperatures, since this reaction needs higher energy of activation than the decomposition into CH_3 and C_2H_4. The study of Rabinovitch, Davis, and Winkler[13] confirms this view. They found CH_4 and C_2H_6 as the main products of reaction between propylene and H atoms produced by Wood-Bonhoeffer technique. This was interpreted by them as a result of a decomposition of a "hot" radical $CH_3\cdot CH_2\cdot CH_2\cdot$ produced by association of C_3H_6 and H. The total balance of products obtained in their investigation leaves no room for the assumption of the reaction (2). For the reason discussed previously, the association of a "hot" radical $CH_3\cdot CH\cdot CH_3$ is of little importance.

However, an increase of the total pressure increases the probability of stabilization of either of these "hot" radicals by subsequent collision with a third body. This conclusion is born out by results obtained by Moore and Taylor[14] who investigated the mercury photosensitized hydrogenation of propylene. The stabilized radicals mainly dimerize giving C_6H_{14} as the main products of reaction. The formation of "non-hot" association products in mercury photosensitized hydrogenation may be still easier because of the participation of HgH molecules as hydrogenation agents. A collision between HgH and C_3H_6 leads to Hg and C_3H_7 radical and the excess energy can be removed in the form of translational energy.

In discussing the reactions involving the "hot" radicals C_3H_7 we have given the reasons why the formation of a "hot" $CH_3\cdot CH\cdot CH_3$ radical is not effective. These reasons do not apply to reactions involving "non-hot" C_3H_7 radicals. The investigation of Moore, reported on the 113th meeting of American Chemical Society (April 1948) shows the preferential formation of $CH_3\cdot CH\cdot CH_3$ radical to that of $CH_3\cdot CH_2\cdot CH_2$. The reported product of reaction was  $CH_3\cdot\underset{\displaystyle CH_3}{\underset{|}{CH}}\cdot\underset{\displaystyle CH_3}{\underset{|}{CH}}\cdot CH_3$ and not *n*-hexane.

CONCLUSIONS

The experimental facts reported in this paper lead to the final conclusion that the first step in the thermal decomposition of propylene is the breaking of the molecule into an H atom and an allyl radical. The H atoms react with the excess of propylene giving H_2, CH_4, and C_2H_4. On that basis we could postulate two mechanisms which account for all observed facts. The fate of the allyl radicals was not finally established. Its decomposition into an H atom and an allene molecule is the basis of mechanism 2, while mechanism 1 assumes its removal by disproportionation.

One can assume a mechanism very similar to mechanism 2, in which the first step is the breaking of a propylene molecule into CH_3 and $CH_2{:}CH$ radicals, followed by the same sequence of reactions as postulated in mechanism 2. The argument against this assumption is based on our results obtained in the study of the thermal decomposition of isobutene (following paper). This compound decomposes according to mechanism 2. If the first step were the splitting-off of a CH_3 radical, then the products would not contain any H_2. The presence of hydrogen proves, therefore, the splitting of isobutene molecules into H atoms and $CH_2\cdot C(CH_3){:}CH_2$ radicals. It is extremely improbable that the initial decomposition of propylene would differ from that of isobutene, and thus we reject the suggested reaction

$$CH_3{:}CH=CH_2\rightarrow CH_3\cdot+\cdot CH=CH_2.$$

The problem of the energy of the $C-H$ bond in propylene would be solved if we could decide between the two mechanisms discussed. Taking into account all the arguments mentioned in the discussion, we are inclined to assume that mechanism 2 with a short chain is the more probable one. On that basis we suggest 78 kcal./mole as the most probable value for $D(C-H)$ in propylene. Further investigations are required, however, before we can reach the final decision.

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[13] B. S. Rabinovitch, S. G. Davis, and C. A. Winkler, Can. J. Research **21B**, 251 (1943).

[14] W. J. Moore and H. S. Taylor, J. Chem. Phys. **8**, 504 (1940).