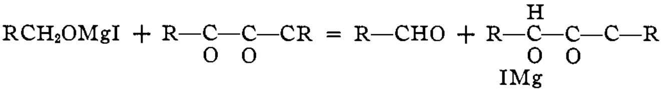
This reaction is reversible, but if, for instance, iodomagnesium benzylate be treated with a susceptible carbonyl compound whose reduction product is not affected by benzaldehyde, then the reaction should go to completion. Benzils are such compounds



$$RCH_2OMgI + R\!-\!\underset{O}{C}\!-\!\underset{O}{C}\!-\!CR = R\!-\!CHO + R\!-\!\overset{H}{\underset{\underset{IMg}{O}}{C}}\!-\!\underset{O}{C}\!-\!C\!-\!R$$

In two experiments of this nature, using benzyl and chlorobenzyl alcohol, respectively, and benzil as the oxidizing compound, we obtained an 85% yield of the corresponding aldehydes and 90% of benzoin.

Summary

To a still greater extent than the iodomagnesium salts of monohydroxy alcohols, the similar salts of hydrobenzoin and of substituted hydrobenzoins have been found effective in reducing saturated and unsaturated, aromatic and aliphatic aldehydes to their corresponding primary alcohols. Only one of the two alcohol groups in the hydrobenzoins is involved in this reaction, the hydrobenzoins becoming oxidized by the aldehydes to benzoins, just as secondary alcohols become oxidized to ketones.

The mechanism of this oxidation-reduction reaction consists in the transfer of an H and MgI from the group >CHOMgI in the alcohol to the carbonyl group of the aldehyde.

The results of this investigation supply further evidence in favor of Marshall's explanation in regard to the apparently anomalous formation of primary alcohols and ketones in the course of the Grignard reaction on aldehydes: namely, the normally produced addition product, RR'CHOMgI, is liable to become oxidized by the excess of aldehyde to the ketone RCOR', and the aldehyde reduced to RCH_2OMgI.

ANN ARBOR, MICHIGAN

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

THE PYROLYSIS OF PROPYLENE[1]

BY CHARLES D. HURD[2] AND RICHARD N. MEINERT[3]

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That hydrocarbons of different types differ quite widely from each other in their behavior on pyrolysis has been demonstrated in earlier papers of this series. Normal and isobutane[4] both undergo primary changes into

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[1] This paper contains results obtained in an investigation on "The Pyrolysis of Pure Hydrocarbons," listed as Project No. 18 of American Petroleum Institute Research. Financial assistance in this work has been received from a research fund of the American Petroleum Institute donated by the Universal Oil Products Company. This fund is being administered by the Institute with the coöperation of the Central Petroleum Committee of the National Research Council.

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[4] Hurd and Spence, THIS JOURNAL, 51, 3353 (1929).

simpler substances. Isobutylene[5] not only yields simpler gaseous products but also gives rise to liquids which are aromatic in character. Methylacetylene was found to rearrange into allene, and allene,[6] in turn, pyrolyzes almost exclusively into allene polymers. These polymers are liquids of an entirely different nature from the liquids produced from isobutylene.

The subject of this study, propylene, has been investigated previously only by Frey and Smith.[7] They observed that about one-third of the propylene was decomposed at 575° with a reaction time of four minutes, in a silica bulb. Among the products of the reaction were hydrogen, ethylene, ethane and propane in small amounts. They also reported the presence of butylene and of small amounts of paraffin hydrocarbons containing as high as eight carbon atoms. The same workers showed that propylene reacts with hydrogen at 575° to form some propane.

Preliminary experiments in this Laboratory[8] indicated that propylene was not appreciably changed at temperatures below 525° in pyrex glass apparatus when the hot contact time was fifty seconds. The present study revealed that there was practically no change below 600° even with contact times of two minutes. At 600° the change was only 4% with a contact time of thirty seconds but it increased to about 30% with a contact time of 158 seconds. At 650° and 120 seconds the amount of propylene pyrolyzed was 60%, while at the same temperature and a contact time of thirty seconds it was 16%. At 700° the change was 51% with a contact time of only twenty-five seconds, but it reached 72.5% by doubling the contact time. In quartz tubes with a contact time of about one-half second, the propylene was 90 to 95% pyrolyzed when the temperature was 900 to 950°. The course of the reaction was similar to the results in pyrex wherein a lower temperature but a longer contact time was used.

The reaction in pyrex was predominantly homogeneous and unimolecular, since dilution of the gas with nitrogen, or creation of an increased surface by packing the tube with pyrex glass, had a negligible effect on the fraction of propylene decomposed in a given time.

The larger part of the propylene which disappeared in the reaction was broken down into simpler gases. Methane, ethylene, hydrogen and paraffins higher than methane (consisting principally of ethane) were found in the ratio of 3:3:1:1. As would be expected, the quantity of methane, hydrogen and total gas was found to increase with increasing temperature or with increasing contact time. This is evidently due not only to a greater extent of pyrolysis but also to secondary reactions which involve the breakdown of C_2 hydrocarbons.

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[5] Hurd and Spence, THIS JOURNAL, **51**, 3561 (1929).

[6] Meinert and Hurd, *ibid.*, **52**, 4540 (1930).

[7] Frey and Smith, *Ind. Eng. Chem.*, **20**, 948 (1928).

[8] Hurd and Spence, unpublished results.

In pyrex or in quartz about one-fifth to one-fourth of the propylene used was converted into aromatic liquids. Benzene and toluene were identified and more complex substances, such as naphthalene and phenanthrene, were indicated. The last two are not considered to be primary products of the pyrolysis since they could arise by interaction of the simpler aromatic hydrocarbons with olefins at the high temperatures in question.

When small volumes of propylene were pyrolyzed no feasible method suggested itself of obtaining the weight of the liquids, but with larger runs this could be done although quantitative precision was, necessarily, not realized. Thus, it was possible to account for the hydrogen within fairly satisfactory limits. In two runs at 700°, the check was 100–104% of the theoretical and in one run at 955° the value was 107%. In one run at 650° only 88% of the hydrogen was accounted for, and in one at 600° the value dropped to 81%. Probably these variations are the result of experimental error due to the smaller quantity of liquid product which was formed in these lower temperature experiments. Similar calculations on the carbon balance were of value in estimating the limit for the quantity of carbon which may have been liberated in the various runs.

When a mixture of approximately equal parts of hydrogen and propylene was pyrolyzed, it was noticed that the amounts of ethylene and methane formed were greatly increased. Little or no propane was formed. This indicates a tendency for the hydrogen to cause a scission of the propylene molecule, thus

$$CH_3{-}CH{=}CH_2 + H_2 \longrightarrow CH_4 + CH_2{=}CH_2$$

Such a reduction may be preceded by the division of propylene into the methyl and vinyl radicals.

The pyrolytic behavior of propylene in monel metal was also investigated. Here the almost exclusive change was a decomposition into hydrogen and a sooty form of carbon. Moreover, the rate of decomposition was much greater than when pyrex or quartz tubes were employed. Thus, with the same hot contact periods, much more propylene decomposed in monel at 350° than in pyrex at 650°.

A peculiarity about the reaction in monel metal was that it was autocatalytic. The carbon formed and deposited on the walls of the tube near the beginning of the experiment catalyzed the reaction so that it proceeded much more rapidly after about twenty minutes. A number of experiments at different temperatures showed conclusively that this was the case. Both in appearance and in quantity was the carbon from the monel tube in decided contrast to the shiny, hard flakes of carbon which were deposited on the walls of the pyrex tube.

The pyrolysis in monel metal tubes started at a temperature of 350°. At 375°, with a contact time of about half a minute, it was practically complete. No liquids or tarry products were formed in the reaction at any temperature from 300 to 650°. About one liter of hydrogen and one-half liter of a mixture of paraffin hydrocarbons resulted from each liter of propylene consumed at 375°. With increasing temperature, the amount of hydrogen formed per liter of propylene increased to 1.7 liters at 650°, while the amount of paraffins (chiefly methane) formed decreased to 0.2 liter.

The fact that the production of hydrogen increased with increasing temperature while the production of paraffins decreased indicates that the first step in the reaction is probably a splitting into compounds that are simpler than propylene, but which are themselves unstable at higher temperatures and also break down into their elements.

Propylene, Isobutylene and Allene Compared.—It is interesting to compare the relative stability in pyrex of propylene and isobutylene, since both are olefin hydrocarbons which have been studied under analogous conditions. In Table I it is shown that at the same temperature and contact time, the amount of pyrolysis is about the same for the two hydrocarbons. The isobutylene data are from the paper of Hurd and Spence.[9]

TABLE I

RELATIVE STABILITY OF PROPYLENE AND ISOBUTYLENE

Isobutylene			Propylene		
Temp., °C.	Contact time, sec.	Extent of pyrolysis, %	Temp., °C.	Contact time, sec.	Extent of pyrolysis, %
600	200	20.0	600	190.0	24.3
650	27	22.7	650	26.8	16.7
			650	30.0	16.0
700	25	51.4	700	25.0	50.8

The mechanism which has been developed for isobutylene adequately explains the data in the pyrolysis of propylene. The former was reported to produce methane, propylene, hydrogen and isobutane at 600° in the ratio (approximately) of 10:5:3:4. At 700° there was more methane and considerably less propylene in the off-gas. From the results obtained in this work, it would be expected that propylene formed from isobutylene would break down rather rapidly at 700°. Aromatic liquids were found to the extent of 23 to 63%, depending on the temperature and the contact time. Similar liquids were formed from propylene in 15–28% yields.

To explain the pyrolysis of *i*-butylene, Hurd and Spence suggested that heat may rupture the single C—C or C—H bonds and that it may activate the C=C double bonds. Gaseous products were regarded as coming from the first process and liquids from the last. Evidently the same mechanism applies with the pyrolysis of propylene. The general experimental data for both propylene and isobutylene were very similar.

Propylene and allene are both C_3 hydrocarbons, but their mode of pyrolysis is quite different. The former is considerably the more stable of

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[9] Hurd and Spence, THIS JOURNAL, 51, 3561 (1929).

the two and it changes into gases and aromatic liquids. The latter gives but small amounts of gases and large quantities of non-aromatic liquids. No allene or polymers of allene were found (except possibly in traces) among the products of pyrolysis of either propylene or isobutylene.

Experimental Part

Apparatus.—An apparatus similar to the one described by Hurd and Spence for use with *i*-butylene[10] was constructed for this study. The dimensions of the various reaction tubes were as follows:

Tube	Total length, cm.	Inside diameter, cm.	Length in furnace, cm.
Pyrex	90	2.5	75
Quartz	85	0.45	75
Monel	92	2.0	75

A 15-cm. length of 7-mm. tubing was sealed into the bottom of the pyrex tube. It was attached to a trap immersed in ice water which served to condense the liquid products of the reaction. The thermocouple was placed inside the pyrex tube and was protected by a pyrex sheath.

Temperature measurements of the quartz tube were made by placing the thermocouple in another quartz tube having walls of the same thickness and having one end closed. The two tubes were suspended side by side in the furnace with the end of the thermocouple about two-thirds of the way down.

With the monel metal tube the thermocouple was placed inside the tube with a porcelain insulator as its only covering. The ends of the thermocouple were exposed directly to the hot gases and the leads were run through the rubber stopper which closed the top end of the tube. To prevent the conduction of heat to the rubber stoppers, tight spiral coils, consisting of right turns of 5-mm. copper tubing, were wound around both ends of the monel tube. With water circulating through these coils the ends of the monel metal tube were kept quite cool by this device.

The gases were analyzed as previously outlined by Hurd and Spence.[11]

Source of Propylene.—The propylene used in these experiments was generously furnished by E. R. Squibb and Sons. Analysis showed that it contained less than 1% of impurities.

The Pryolysis of Propylene in Pyrex.—Preliminary experiments, with temperature varying between 550 and 700° and the contact time varying between twenty-five and one hundred fifty seconds, were made to determine the best conditions for the pyrolysis. The results are given in Table II, and the data make it evident that increasing either the temperature or the contact time gives rise to a marked increase in the amount of propylene decomposed. The results show further that the temperature range between 600 and 700° offers the best opportunity for studying the mechanism of the reaction. Below 600° the pyrolysis is negligible, while above 700° the reaction is complicated by secondary reactions, consisting of the decomposition of the products of the primary reactions.

It will be noted that the relative amounts of the various products formed

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[10] Hurd and Spence, This Journal, **51**, 3562–3563 (1929).

[11] Hurd and Spence, *ibid.*, **51**, 3356–3357 (1929).

TABLE II

EFFECT OF TEMPERATURE AND RATE OF FLOW

Run number	2	3	4	6	5	7	8
Temperature, °C.	600	650	700	550	600	650	700
Contact time, sec.	29	30	25	137	158	120	52.4
Decomposition, %	3.9	16	50.8	4.1	29.7	59.3	72.5
Cc. of products formed per liter of propylene pyrolyzed							
Absorbed in 62.5% H_2SO_4	...	59	24	...	7	0	0
Acetylenes	...	32	11	...	16	6	0
Ethylene	...	314	396	...	269	323	438
Hydrogen	...	83	149	...	69	127	152
Paraffins	...	415	558	...	375	637	580

from each liter of propylene pyrolyzed are not greatly affected either by changing the temperature or the contact time. This matter will be discussed in more detail in a later section.

Effect of Dilution on the Reaction.—Several runs were made with either hydrogen or nitrogen added to the propylene in order to find out the effect of dilution of the propylene. The results are shown in Table III.

TABLE III

EFFECT OF DILUTION ON THE PYROLYSIS OF PROPYLENE

Run number	5	12	11	10
Temperature	600°	600°	600°	600°
Contact time, sec.	158	158	125	125
Per cent. propylene in entering gas	97	53.1	97	56.6
Per cent. N_2 in entering gas	00	45.7	00	00
Per cent. H_2 in entering gas	00	00	00	39.1
Per cent. propylene pyrolyzed	29.7	23.3	26.7	29.5
Products formed per liter of propylene pyrolyzed, cc.				
Gas removed by 62.5% H_2SO_4	7	12	22	00
Acetylenes	16	16	49	22
Ethylene	269	428	340	560
Hydrogen	69	130	119	[a]
Paraffins	375	500	388	747
n in C_nH_{2n+2}	1.54	1.42	1.42	1.25

[a] 387 cc. of hydrogen were used up for each liter of propylene pyrolyzed.

Examination of Runs 5 and 12 shows a somewhat smaller percentage of pyrolysis in the latter case. Whether or not this is a significant difference is open to question since in high temperature experiments which are carried out under seemingly identical conditions it is the customary experience that precise duplication of data is only rarely achieved. We are inclined to believe that the values 29 and 23 are sufficiently near each other to indicate a predominantly unimolecular reaction, although strict interpretation of the values would indicate a reaction order between first and second. Some of the other differences which are noticeable in these two runs may be accounted for by the fact that in Run 12 almost no liquid reaction products were formed whereas in Run 5, with no dilution, about 20% of the propylene pyrolyzed was recovered as liquids. The nitrogen would act to lessen the formation of liquids by diluting the primary reaction products and hindering them from undergoing polymerization.

When Runs 10 and 11 are compared, the percentage of pyrolysis is a little higher (rather than lower) in the dilution experiment. The order of magnitude is similar, however. As in the nitrogen dilution experiment, the amounts of ethylene and of paraffins formed are much larger than in runs where there was no dilution. Again, with a smaller liquid yield, the gaseous products showed up correspondingly when calculated on the basis of cc. of each product formed per liter of propylene pyrolyzed.

A striking result when Runs 11 and 10 are compared is the change in the *n* in the paraffin formula. The volume of the paraffins formed is greatly increased, relatively more so than the volume of ethylene, but the *n* is decreased by adding hydrogen to the entering gas. This indicates the formation of methane, probably by hydrogenation of the CH_3- radicals formed when the propylene is split at the single bond. Apparently not much propylene is hydrogenated to propane; otherwise the *n* would be higher than it is. This is an important point when considering the mechanism of the reaction, for it is best interpreted by considering that the CH_3- residue is present in the hot zone, at least momentarily.

Effect of Increased Surface.—Experiments were made at 600 and 650° to determine whether or not increasing the surface in the reaction tube had any effect on the amount of propylene pyrolyzed. The method consisted of packing the tube with long pieces of capillary tubing made by heating sections of large capillary tubing and drawing them out to a diameter of about one millimeter. Rough calculation showed that the surface in the reaction tube was about trebled. Table IV shows the results of the experiments. The calculation for the contact time took account of the decrease in the volume of the tube due to the packing. Evidently the increased surface in the tube had no appreciable effect upon the amount of propylene pyrolyzed. Therefore, the decomposition of propylene is apparently unimolecular and homogeneous.

TABLE IV

EFFECT OF INCREASED SURFACE

	Unpacked	Packed	Unpacked	Packed
Run number	20	25	21	26
Temperature, °C.	600	600	650	650
Contact time, sec.	139	150	90.2	115
Percentage pyrolysis	18.7	17.0	41.8	44.2

Gaseous Products Obtained in the Reaction.—The gaseous products of the pyrolysis of propylene were measured, collected and analyzed. From the percentage of propylene in the off-gas, the amount of undecomposed propylene was determined, and this, subtracted from the propylene passed into the tube, gave the amount of propylene changed in the pyrolysis. The percentage of pyrolysis could then be readily calculated.

From the analysis of the off-gas and the volume of the off-gas, the total volume of each component present was found. This was divided by the number of liters of propylene actually changed and the result expressed as the number of cc. of each component per liter of propylene pyrolyzed. The advantage of this method of calculating the results is apparent, for it puts all the experimental data on a common basis.

Table V shows some of the representative data at various temperatures and contact times. The table includes data with both pyrex and quartz reaction tubes.

TABLE V

PRODUCTS OBTAINED FROM PROPYLENE PYROLYZED IN PYREX AND QUARTZ

Run number	5	11	24	3	7	23	4	8	28	29
Tube, pyrex or quartz	P	P	P	P	P	P	P	P	Q	Q
Temp., °C.	600	600	600	650	650	650	700	700	950	955
Contact time, sec.	158	125	131	30	120	79	25	53	0.513	0.471
Entering flow, cc./min.	43	52	51	217	53	80	237	115	311	339
Exit flow, cc./min.	39	51	50	207	55	80	261	130	436	478
Press. in tube, mm.	744	750	752	748	746	750	744	742	744	750
Vol. entering gas, l.	9.56	23.3	3.73	23.9	10.1	3.84	24.9	13.7	12.44	17.96
Vol. exit gas, l.	8.87	22.7	3.63	23.7	10.5	3.85	26.8	15.5	17.45	25.33
C_3H_6 in entering gas, %	94.9	96.8	95.9	96.6	95.3	95.9	94.2	95.2	95.0	95.0
Composition of exit gas, percentage by volume										
Acetylenes	1.3	1.5	0.0	0.9	1.1	1.1	1.8	1.4	2.2	2.4
Absorbed in 62.5% H_2SO_4	1.3	1.4	0.0	2.1	0.9	1.1	2.1	0.6	1.2	0.3
Propylene	71.9	72.6	83.4	82.0	37.1	59.2	43.0	23.0	6.7	3.3
Ethylene	8.2	9.0	5.2	4.9	17.5	12.9	17.7	26.7	23.5	24.4
Hydrogen	2.1	2.9	1.3	1.3	6.9	4.3	6.6	9.3	22.0	24.7
Paraffins	11.4	10.3	6.4	6.5	34.5	18.6	24.8	35.2	41.0	43.2
n in C_nH_{2n+2}	1.5	1.42	1.54	1.3	1.25	1.29	1.2	1.16	1.05	1.09
Carbon monoxide	0.4	1.0	0.2	0.5	0.6	0.2	0.0	1.1	....	....
Carbon dioxide	.4	0.0	.0	.2	.1	.3	.3	.2	....	....
CO + CO_2	....	....	....	...	....	....	...	....	0.9	0.8
Pyrolysis, %	29.7	26.7	15.5	16.0	59.3	38.4	50.8	72.5	90.3	95.2
Cc. of gaseous products formed per liter of propylene entering										
Acetylenes	5	13	....	5	4	....	6	....	31.8	34.8
Absorbed in 62.5% H_2SO_4	2	6	....	9	3	....	12	....	17.4	3.8
Ethylene	80	91	53	50	192	134	202	318	343.0	354.5
Hydrogen	21	32	13	13	76	45	76	111	318.0	359.0
Paraffins	112	104	65	67	378	194	283	420	593	628
Cc. of gaseous products per liter of propylene pyrolyzed										
Acetylenes	16	49	....	32	6	....	11	....	35.2	36.6
Absorbed in 62.5% H_2SO_4	7.	22	....	59	5	....	24	....	19.3	4.0
Ethylene	269	340	340	314	323	350	396	438	379.6	372.7
Hydrogen	69	119	85	83	127	117	149	152	352.3	377.3
Paraffins	375	388	418	415	637	505	558	580	656.5	659.9
Wt. of liquids, g.	Trace	2.37	....	Trace	1.7	....	6.9	3.8	....	6.47
Per cent. of liquids, by wt. of C_3H_6, pyrolyzed	....	21	....	...	15.4	....	27.6	24	....	20.8

Sufficiently large samples of propylene were used in Runs 11, 7, 4, 8 and 29 so that it was possible to check the hydrogen (free or combined) in the final gaseous products with the combined hydrogen in the original propylene, correction being made in the latter for the propylene which was found to change into liquid products. In these runs the liquid could be weighed satisfactorily although high precision in this regard was impossible. This, no doubt, was the major cause for the discrepancies which were noted in the hydrogen balance. In Runs 5, 24, 3 and 23 the original quantity of propylene was too small to yield a satisfactory volume of liquid. In Run 28 the liquid product was not worked up.

In Run 11, 1906 out of a possible 2370 units of hydrogen were found in the gaseous products per liter of propylene pyrolyzed; in Run 7, 2233 out of 2538; in 4, 2276 out of 2172; in 8, 2281 out of 2280; and in 29, 2553 out of 2376. In making these calculations, the gas which was "absorbed in 62.5% H_2SO_4" was assumed (with no especial justification) to be C_4H_8, and the "acetylenes" were assumed to be C_2H_2. To illustrate the method of calculation in Run 11, 49 cc. of $C_2H_2 \approx$ 49 cc. of H_2; 22 cc. of $C_4H_8 \approx$ 88 cc. of H_2; 340 cc. of $C_2H_4 \approx$ 680 cc. of H_2; 388 cc. of C_nH_{2n+2} where $n = 1.42 \approx$ 970 cc. of H_2, which with 119 cc. of H_2 totals 1906 cc. Supposedly, this volume originated from 79% of 1000 cc. of C_3H_6, which is equivalent to 2370 cc. of hydrogen. The check is only 81% of the theoretical, but in the other four cases it is better, namely, 88, 104, 100 and 107%.

The carbon content of the gaseous products was always less than the carbon content of the original propylene, corrected as before for the portion which changed into liquids. The two chief causes for this difference were carbon formation and the experimental difficulty in collecting and weighing the small volume of liquid. Thus, in Runs 11, 7, 4, 8 and 29 the units of carbon in the gas at the end and at the beginning, respectively, were 1417/2370, 1474/2538, 1580/2172, 1514/2280, 1553/2376. If these differences are interpreted as being solely due to carbon formation, the values would indicate, respectively, 0.51, 0.57, 0.32, 0.41 and 0.45 g. of carbon.

The Liquid Portion.—In addition to the gaseous products, about 20% by weight of each liter of propylene pyrolyzed was recovered as liquid products. In the cases where the temperatures were low and the contact time short, the decomposition of the propylene was very small; consequently it was difficult to weigh the liquids which were obtained, as they amounted to less than a gram, and some of the liquid stuck to the walls of the reaction tube. But with three runs, one at 650° with a contact time of 150 seconds, and two at 700° and a contact time of thirty-six and fifty-two seconds, respectively, several grams of liquids were obtained and these runs averaged a liquid formation of 22% by weight of the propylene actually pyrolyzed.

A portion (12.5 g.) of these liquids, being the aggregate of several runs, was fractionated with a Vigreux fractionating column. The results were as follows.

Fraction number	Boiling point, °C.	Weight, g.
1	70–85	2.34
2	85–107	2.04
3	107–160	2.41
4	160–200	1.58
5	200–210	0.90
Residue		2.90
Loss		0.31
		12.48

Fraction 5 partially solidified on cooling. All these fractions had an aromatic odor resembling that of toluene.

Fractions 1, 2 and 3 were fractionated into three fractions and the refractive indices of these portions were determined. For reference, the refractive index of benzene, n_D^{20}, is 1.501, and for toluene, 1.495.

Fraction	Boiling point, °C.	n_D^{20}
A	75	1.490
B	75–85	1.499
C	85–128	1.502

Most of the fraction B boiled between 83 and 85° and most of fraction C boiled above 118°. The refractive indices, together with the boiling points, indicate that these compounds are aromatic, presumably benzene and toluene with some higher homologs. Fraction A and B nitrated readily and, in experiments described below, it was confirmed that the former was the nitro derivative of benzene. The higher-boiling fractions could not be obtained pure and were not identified.

Besides the gaseous and liquid products, there was always a thin deposit of carbon formed in the reaction tube. This carbon was in the form of graphite and could be removed by scraping it from the tube, but it was more completely removed before each run by burning it out. There was also a small amount of heavy tar which collected on the sides of the tube, which was removed from time to time by dissolving it out with acetone.

The Effect of Shorter Contact Times and Higher Temperatures upon the Pyrolysis of Propylene.—The results are summarized in Runs 25 and 26 of Table V. A quartz tube was used instead of the pyrex tube. The gas was passed through the apparatus as rapidly as possible so that the hot contact time would be very short. The temperature was 950°. This was the maximum temperature of the furnace.

Comparison of these runs with the others shows that pyrolysis at 950° in quartz with a hot contact time of one-half second gives about the same results as pyrolysis at 700° in pyrex with a contact time of fifty-three seconds. The percentage of propylene pyrolyzed is about 90 instead of 73, but the products formed are very much the same. There is about the same percentage of unrecovered propylene which is converted into liquids in each case, *viz.*, 20–25%. In both cases liquids are aromatic hydrocarbons and in both the gaseous products are the same. More hydrogen and methane are formed at the higher temperatures but this would be expected, since the secondary reactions would also be more rapid at high temperatures.

The liquids obtained from the 950° experiments were fractionally distilled as carefully as the small volume would permit, with these results.

Fraction	Volume, cc.	B. p., °C.	n_D^{20}
A	2.0	78–97	1.5025
B	0.8	97–130	1.5140
C	1.0	130–180	1.5465

Fraction A had an odor very much like that of benzene, fraction B an odor somewhat resembling that of toluene and fraction C smelled like tar. The properties of these liquids were almost identical with those of the liquids obtained from propylene in pyrex apparatus at 700°. Nitration of fraction A yielded *m*-dinitrobenzene.

Experiments with a Monel Metal Tube.—A summary of data is given in Table VI. It will be seen that the effluent reaction products were gaseous, but in addition there was always a large amount of carbon deposited in the tube. In some cases this deposit was so thick that it closed

TABLE VI

PRODUCTS OBTAINED FROM PROPYLENE IN MONEL METAL TUBE

Run	1	2	3	4	5	6	7
Temp., °C.	650	500	375	250	325	350	400
Contact time, sec.	14.8	35.3	27.3	22.7	26.5	25.8	10.5
Entering flow, cc./min.	174	90	139	207	169	166	377
Exit flow, cc./min.	362	175	225	207	170	220	523
Press. in tube, mm.	745	748	752	742	748	745	741
Vol. entering gas, l.	5.32	2.25	7.63	16.55	10.68	6.65	11.30
Vol. exit gas, l.	11.05	4.38	12.35	16.55	10.77	8.80	15.6
C_3H_6 in entering gas, %	94.7	94.7	94.7	94.7	94.7	94.7	94.75
Composition of exit gas, percentage by volume							
Hydrogen	77.6	71.3	56.8	. . .	....	38.3	39.9
Propylene	2.9	1.0	4.8	93.7	94.3	37.6	46.2
Ethylene	2.4	1.0	0.6	....	....	0.3	1.0
Other unsatd. hydrocarbons	1.1	2.0	2.1	. . .	....	0.5	1.2
Paraffins	9.2	13.0	30.0	....	....	21.7	9.1
n in C_nH_{2n+2}	1.26	1.50	1.54	. . .	. . .	1.81	1.83
Percentage pyrolysis	93.6	92.7	91.2	0.0	0.5	47.4	32.4

TABLE VI (*Concluded*)

Gaseous products formed per liter of propylene entering, cc.							
Hydrogen	1620	1390	976	....	....	535	583
Paraffins	192	253	514	....	....	303	133
Ethylene	60	19	10	....	....	4.2	14
Other unsatd. hydrocarbons	27	39	35	....	....	7	17
Gaseous products formed per liter of propylene pyrolyzed, cc.							
Hydrogen	1730	1500	1070	....	...	1128	1800
Paraffins	205	273	564	...	...	638	411
Ethylene	64	21	11	....	....	9	45
Other unsatd. hydrocarbons	29	42	38	....	....	15	54

the tube completely and stopped the flow of the gas. This carbon was not graphitic as was the carbon deposited when propylene was pyrolyzed in a pyrex tube, but it had the appearance of soot and could be scraped easily from the walls of the tube. No liquids were obtained.

It was noticed in these experiments that the ratio of the off-gas to the entering gas began to increase after the first five or ten minutes of the run and finally reached a constant value. This points to the fact that the action is autocatalytic, the carbon deposited on the walls acting as the

TABLE VII

RATIO OF OFF-GAS TO ENTERING GAS IN MONEL METAL

Time	Entering volume	(*a*)	Exit volume	(*b*)	Ratio *b*/*a*	Time	Entering volume	(*a*)	Exit volume	(*b*)	Ratio *b*/*a*
		Run 1, 650°						Run 3, 375°			
0	0.000	...	0.000	...	..	0	0.000	...	0.000	...	..
3	.020	0.020	.032	0.032	1.60	3	.015	0.015	.015	0.015	1.00
8	.057	.037	.106	.074	2.00	13	.072	.057	.077	.062	1.09
13	.097	.040	.185	.079	1.97	18	.102	.030	.117	.040	1.33
23	.161	.064	.341	.156	2.44	28	.160	.058	.202	.085	1.46
28	.190	.029	.407	.066	2.27	38	.220	.060	.294	.092	1.53
30	.198	.008	.424	.017	2.13	43	.248	.028	.344	.050	1.78
						53	.306	.058	.440	.096	1.66
						63	.362	.056	.537	.097	1.73
						68	.394	.032	.591	.054	1.69
		Run 6, 350°						Run 7, 400°			
0	0.000	...	0.000	...	..	0	0.000	...	.000	...	..
5	.033	0.033	.036	0.036	1.09	4	.055	0.055	.055	0.055	1.00
10	.069	.036	.074	.038	1.05	9	.127	.072	.128	.073	1.01
15	.104	.035	.111	.037	1.06	14	.200	.073	.200	.072	0.99
30	.197	.093	.222	.111	1.20	19	.272	.072	.275	.075	1.04
35	.227	.030	.261	.039	1.30	24	.343	.071	.362	.087	1.22
40	.260	.033	.306	.045	1.36	29	.415	.072	.458	.096	1.33
45	.295	.035	.353	.047	1.34	34	.490	.073	.560	.102	1.36
50	.327	.032	.399	.046	1.43	39	.565	.075	.667	.107	1.43
55	.357	.030	.445	.046	1.53	44	.638	.073	.771	.104	1.43
						49	.712	.074	.872	.101	1.37

catalyst so that the full rate of the reaction is not reached until the tube has been coated with carbon. The increase of the ratio of the off-gas to the entering gas is shown in Table VII. The data are given as taken from Runs 1, 3, 6 and 7. In the first column the elapsed time from the beginning of the run is given; in the second column, the total volume of the entering gas from the beginning of the run and in the fourth column the total volume of the off-gas from the beginning of the run. The figures in column three, (*a*), represent the differences between successive figures in column two. Similarly, column five, (*b*), gives the differences between the readings in the fourth column. The ratio b/a, given in column six, represents the ratio of off-gas to entering gas over the period of time between successive readings of the wet-test meters which measured the entering and exit volumes. It is to be noted that these readings were not taken at regular intervals but this does not affect the ratios.

It can be seen readily that the ratios increase until a maximum is reached, and the maximum is reached in a shorter time at high temperatures than at low temperatures.

All the volumes in Table VII are expressed in cubic feet. The time is in minutes.

Summary

Propylene is rapidly decomposed at temperatures above 600° in pyrex or quartz. The gaseous products are largely hydrogen, methane and ethylene with smaller amounts of acetylene and ethane. Aromatic liquids (benzene, toluene, etc.), comprise approximately 25% of the total reaction products. The reaction has been shown to be predominantly homogeneous and unimolecular. A mechanism for the reaction is suggested.

Under comparable conditions in monel metal, decomposition of propylene begins at a much lower temperature, namely, 350°. The products are largely carbon and hydrogen and the reaction is autocatalytic.

As compared with isobutylene, propylene has been shown to undergo an almost identical type of pyrolysis.

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