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THE DECOMPOSITION OF METHANE
INDUCED BY FREE RADICALS

by

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THE DECOMPOSITION OF METHANE

INDUCED BY FREE RADICALS

Introduction:

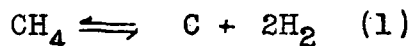
The object of this research was to investigate the effect of free radicals on the decomposition of methane in the temperature range 400-550°C. It was thought possible that the presence of free radicals might cause partial decomposition of the methane with the formation of appreciable quantities of unsaturated compounds such as ethylene. The source of the free radicals was dimethyl acetal, a diether.

Since consideration of the normal pyrolysis of methane is necessary, the next few pages will deal with this and other topics pertinent to the problem.

I. THE THERMAL DECOMPOSITION OF METHANE:

Methane (CH_4) is the simplest of the paraffin group of hydrocarbons and the most common. Its properties and its reactions, in particular its thermal decomposition, have been very thoroughly studied and a large amount of data has been collected. An exhaustive discussion of the literature is given by G. Egloff (1).

The mechanism of the decomposition of methane is the most important consideration for the purposes of this thesis. Methane decomposes ultimately into carbon and hydrogen, setting up an equilibrium of the form



From this fact and the free energy of formation of methane, it is possible to calculate the percent hydrogen in equilibrium with methane at a given temperature. Parks and Huffman (2) have carried this out and Table I shows the percentage hydrogen in an equilibrium mixture at one atmosphere total pressure at various temperatures.

TABLE I:

<u>Temp. °K</u>	<u>ΔF</u>	<u>% H₂ (by volume)</u>
600	-5,690	8.8
700	-3,380	25.6
800	-1,050	50.6
900	+1,290	73.7
1000	+3,360	87.6
1100	+5,945	94.2

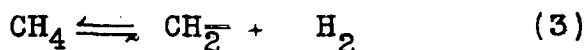
Equilibrium is attained only in the presence of a catalyst. When catalysts such as nickel or iron are used, however, the relative proportions of hydrogen and methane observed experimentally are found to be of the same order of magnitude as those predicted theoretically.

The path of the decomposition, which is complicated,

has been studied very carefully by a number of workers but there is still some difference of opinion concerning it. Holliday and Goodarham decomposed methane by the flow method (3) and found that the partial pressure of acetylene in the reaction products was always fairly constant. They assumed, therefore, that the initial reaction was the homogeneous and bimolecular formation of acetylene:

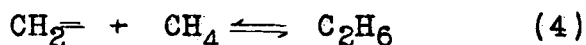


Kassel then pointed out (4) that their rates of reaction were 10^5 times as great as the calculated value for a reaction that was bimolecular and possessed a minimum energy of activation of 91,000 calories per mol. He studied the thermal decomposition of methane in quartz bulbs at 700-850°C, obtaining rate measurements. He considered the initial reaction to be homogeneous and kinetically first order. The primary process was the unimolecular reaction:

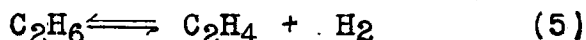


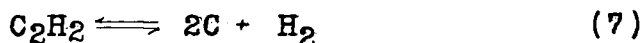
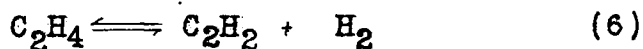
with a rate constant of $5 \times 10^{11} e^{-79385}$

The observed rate constant is twice this, from which Kassel assumes the next step to be:



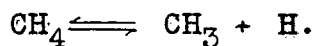
He then postulated that the succeeding reactions were successive dehydrogenation of the ethane to carbon:





Reactions (5) and (7) above have been confirmed experimentally. Equation (6) was difficult to confirm because of the complicated products arising from pyrolysis of ethylene. Kassel found a relationship between rate and concentration of hydrogen. He considered that this complex hydrogen dependence was explained by his theory and by supposing that all the reactions concerned were reversible.

Belchetz (7) decomposed methane on a platinum filament at 1000°C, adapting Paneth's flow method for detection of free radicals, with mirrors of iodine. He considered that methylene iodide was formed, confirming the presence of methylene radicals and Kassel's theory. Rice and Dooley (8) performed a similar experiment in which they detected the presence of dimethyl ditelluride. On the basis of their work they postulated the initial split of the methane molecule to be:



Kassel, however, considered (6) that the experimental kinetics of methane decomposition could not be explained by any mechanism which involved methyl radicals. He also pointed out some possible sources of error in the experimental methods of Rice and Dooley and reaffirmed his previous conclusions. He was later confirmed by

the work of Belchetz and Rideal (9), who studied the primary decomposition of methane on both platinum and carbon filaments. Using sounder analytical techniques they were able to prove definitely that methylene, not methyl, radicals were formed.

The formation of ethane and its subsequent dehydrogenation was partly confirmed by Storch (28). When he passed methane at low pressure through a carbon filament lamp immersed in liquid nitrogen (-195°C), 95 percent of the methane that decomposed formed ethane; but at the temperature of liquid oxygen (-182.5°C) ethylene was largely formed. With the bulb at the temperature of ice or solid carbon dioxide the only products were carbon and hydrogen.

Staveley and Hinshelwood (10) have proved that methane decomposition is partly a chain mechanism. Introducing nitric oxide into the system slowed down the reaction. The nitric oxide inhibits the chain mechanism, presumably by combining with the free radicals and thus breaking the chain.

There are a large number of catalysts which accelerate the decomposition of methane to carbon and hydrogen; among them are iron, nickel, palladium, and a number of oxides. It has also been claimed that certain higher hydrocarbons are produced by the catalytic treatment of methane (1).

Since the decomposition of methane is governed by a rate mechanism and the several steps by as many equilibria, variation of time and degree of heating produces a great variety of products. Incomplete decomposition at 800-1000°C tends to produce olefins, at higher temperatures, acetylenes. In addition various aromatic compounds, oils, and tars may be formed.

From the free energies of methane and ethylene at 550°C it was possible to calculate the amount of ethylene that would be in equilibrium with the methane, if equilibrium conditions existed. For a total pressure of 30cm., the equilibrium pressure of the ethylene is 10^{-4} cm.

II. REACTIONS INDUCED BY FREE RADICALS:

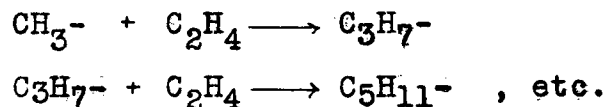
Although the existence of free radicals had been postulated to explain a great number of reactions, it was not until 1929 that Paneth showed that metal alkyls decomposed upon heating into metal atoms and free radicals. His technique was extended to the study of organic compounds by F. O. Rice (23), who attempted to prove that the pyrolysis of most organic compounds proceeded through a free radical mechanism rather than by complicated internal rearrangements. A decomposition involving free radicals proceeds by a chain mechanism. Now a radical may react with a molecule forming a new and heavier radical, or it may split off a molecule and form a new and lighter radical. Since the two types of behavior can

take place alternately, a complicated reaction chain is set up in which the presence of a small number of radicals plays an integral part in the decomposition of a large number of the molecules of the original compound. The chain is broken when two radicals unite or when they are inactivated by coming into contact with certain substances such as nitric oxide.

The initial formation of free radicals by a decomposing compound requires a certain amount of energy. The energy content of the radicals formed is then sufficient to complete the reaction. Thus, if free radicals are introduced into a system containing a compound which is thermodynamically unstable but whose rate of decomposition is slow because of the activation energy barrier, decomposition can frequently be produced at much lower temperature than that at which it would ordinarily occur. A number of compounds produce large quantities of free radicals upon decomposition at fairly low temperatures, among them azomethane, ethylene oxide, and the alkyl metals, and, apparently, dimethyl acetal. Frey (24), and Echols and Pease (25) both studied the induced decomposition of paraffin hydrocarbons. Rice and Polly (26) studied the effect of oxygen and azomethane on n-butane and other substances and found that chain lengths up to several hundred were produced.

Polymerization of ethylene is greatly accelerated

by the pressure of free radicals. Beeck and Rust (27) studied this effect using tetramethyl and tetraethyl lead. They found that ethylene polymerized by successive additions of the olefin molecules to radicals through a bimolecular reaction:



This reaction is a complicating factor in deducing the effect of free radicals on the decomposition of the methane. Some data as to the effect of temperature on this induced polymerization would be of great value, but apparently no work has been done on it.

The Decomposition of Dimethyl Acetal.

The compound used as the source of free radicals was dimethyl acetal. The decomposition of dimethyl acetal was investigated by G. H. Turner at the University of British Columbia in 1940 and 1941. (5) He suggests a primary split into methyl vinyl ether and methanol, followed by secondary splitting of the ether into ethylene, carbon monoxide or methane, or, alternately, by another path into ethylene, carbon monoxide, and hydrogen. Turner's conclusion that free radicals are produced in the acetal decomposition is justified by his experiments showing that the acetal both accelerated the polymerization of ethylene and the decomposition of acetaldehyde.

In the present investigation it proved necessary

to run gas analyses on the decomposition products of dimethyl acetal. There were indications that considerable amounts of ethane were present, which fact might modify the conclusions somewhat. These gas analyses seem to show that more than one mechanism is involved in the decomposition, since approximately 3 percent hydrogen was found at 400°C compared with 12 percent at 550°C, whereas the same increase in temperature reduced the proportion of carbon dioxide from 4.3 percent to 0.6 percent and the proportion of ethylene from 10.6 percent to 1.6 percent. The factor of polymerization probably entered into the latter case.

III. EXPERIMENTAL:

Description of Apparatus:

The essential apparatus has been described in adequate detail by Turner (5) and by Pierce (11); the reader is referred to these two theses for diagrams and descriptions. The only modifications made were the addition of a bulb for storing methane and a manometer for measuring the approximate pressure of methane in the reaction system.

The circuit for temperature measurement and control has also been described (5). Some difficulty was experienced with the photo-relay - partly because of a defective photo tube and partly because of variations in the line voltage. The procuring of a new tube and alterations in the circuit of the relay removed the first difficulty. The source of the 110 volt A.C. current was always overloaded, however, producing large and unpredictable variations in line voltage and hence in heating of the oven. To compensate for these variations there had to be a spread of 0.2 amperes between the upper and lower limits of the current. Thus there was a lag between the action of the relay and the resulting decrease or increase in temperature. The relay would hold the variation in temperature to $\pm 0.4^{\circ}\text{C}$, but its performance within narrower limits could not be relied upon.

The sensitivity of the relay was increased as much as possible by making light from the galvanometer mirror pass through a narrow slit in the window of the relay and by shielding the window with a tube of black paper. Both measures were intended to decrease the amount of stray light reaching the photo-tube.

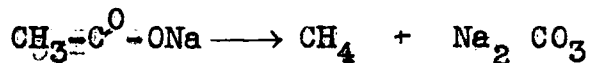
Preparation of Dimethyl Acetal:

The method used was that of Adkins and Nissen (13) as described by Turner (5). The product was distilled twice from sodium and not fractionated further since the second distillation showed a constant boiling point.

Preparation of Methane:

Three methods for the preparation of methane were investigated:

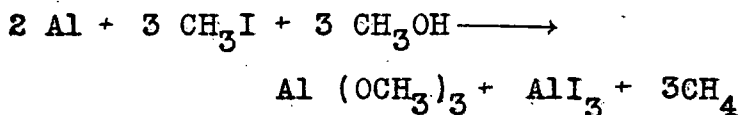
(1) The first was the familiar laboratory method in which sodium acetate and soda lime are heated together, evolving methane according to the reaction:



The sodium acetate used was Baker's C.P., fused just before use, and cooled in a desiccator. The soda lime was prepared by slaking 50 grams of calcium oxide (Baker's) with 50 grams of sodium hydroxide dissolved in 80ml. of water. The resulting slurry was dried over a Bunsen burner for five hours and then the product was pulverized,

Equal quantities of sodium acetate and soda lime were mixed together in a mortar and heated in a thick-walled pyrex tube. The stream of gas was passed through potassium hydroxide solution and then through sulphuric acid containing nickel and silver sulphates to remove unsaturated compounds (14). Analysis of the resulting gas showed no carbon monoxide or dioxide, and no illuminants, but 12 percent hydrogen. The combustion analysis for methane gave erratic results, but there was definite evidence that hydrocarbons or other carbon compounds were mixed with the methane. Since repeated trials in which the composition of the reacting mixture and the degree of heating were varied gave little better results, the method was discarded.

(2) The second method tried was that developed by Bone and Wheeler (15) in which methane is prepared by the action of an amalgamated aluminum couple on methyl iodide and methyl alcohol.



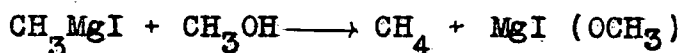
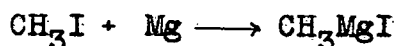
A 50 c.c. round-bottomed flask was half-filled with clean aluminum foil (5 gm), cut into small pieces. Mercuric chloride solution was poured over the foil, poured off after a minute, and the foil washed three times with methanol. 15 gm of methyl iodide were poured onto the couple and a mixture of two parts methyl iodide and one part methanol added dropwise from a tap funnel. The reaction

flask was cooled in an ice bath. The gas evolved passed through a worm in a second ice bath, a concentrated sodium methylate solution, concentrated sulphuric acid, and finally through a trap cooled by ether and dry ice to remove any remaining traces of liquid products. The analysis of the gas showed:



The large proportion of hydrogen was unsatisfactory. It could not be eliminated and was probably due to some impurity in the aluminum. Besides this disadvantage, the reaction was difficult to control, being almost explosive at the beginning. Also the stream of gas tended to carry methyl iodide along with it as shown by the pink colour which always appeared in the sulphuric acid, and by the smell of iodine if the gas were burnt. Since methyl iodide is a catalyst in many decomposition reactions, its presence was undesirable. For these reasons this method was not used.

(3) The method finally adopted was the reaction of the Grignard reagent, methyl magnesium iodide, with methanol.



The methyl iodide was an Eastman Kodak product and the methanol Baker's Absolute.

The methyl magnesium iodide was made by the reaction of 88 grams of methyl iodide with 20 grams of magnesium in 250 c.c. of dry diethyl ether. After completion of the reaction, the product in ether solution was filtered with suction through sintered glass and stored in a glass-stoppered bottle in a desiccator.

Methane was prepared as follows: 50 c.c. of the methyl magnesium iodide solution was placed in a 100 c.c. flask, cooled in an ice bath. Methanol was added, a drop at a time. The methane evolved was passed through two consecutive traps filled with sulphuric acid and glass wool to remove the ether, and through an ether and dry ice trap to remove any last traces of liquid substances. The methane then passed into a second trap. While the train was being cleared of air, the methane passed through this second trap and out of the train. After the train had been cleared, the stopcock leading out of the train was closed and at the same time the second trap was cooled with liquid air, thus liquefying the methane as it was evolved. After about 3 liters of methane had been collected, the trap was cut off from the rest of the train. The liquid methane was then vaporized. The first third was discarded, the middle third was passed into the evacuated storage bulb, and the final third discarded. The small amount of air remaining was removed by vaporization, liquefaction and pumping. This procedure was

repeated until the vapor pressure of methane above the liquid air became constant.

Methane prepared in this manner contained no carbon monoxide or dioxide, no illuminants, no hydrogen, and, as far as could be determined, no ethane or ethers. The analysis for methane showed 98 percent or better.

Methane was twice prepared in the above manner. The first sample was used in runs 1, 3, 5, and 7. The second sample was used in runs 9 and 10.

An attempt was made to prepare methyl magnesium iodide in xylene instead of ether, with the object of eliminating all the precautions required for removal of the ether from the gas. Solvents with high boiling points which have been suggested for this purpose are, isoamyl ether, anisole, and xylene by Gatterman (16 - p 84) and toluene by Hibbert and Sudborough (17). Xylene was used, since it was the only solvent available. Weighing of the unused magnesium indicated that the reaction went about 60 percent to completion. On standing, however, the Grignard reagent separated into two layers, the upper of xylene, the lower a semi-solid layer containing most of the methyl magnesium iodide; and so the reagent could not be used.

Method of Making a Run:

A sealed tube of dimethyl acetal, prepared as des-

cribed by Turner (5) was fixed in position in the apparatus, and the system was pumped down to 10^{-5} cm., an operation requiring about twenty minutes. If methane was required for the run, gas from the storage bulb was passed into the reaction chamber until a pressure of approximately 30 cm. was built up as indicated by the manometer. The stopcock between the reaction chamber and the rest of the system was closed and the mercury level raised to a point just below the level of the constriction. Readings to determine the initial pressure of the methane were taken at this point. Then the acetal tube was broken and the decomposition of the acetal and possible reaction with the methane followed by the variation of pressure with time. The subsequent procedure for the handling of liquid and gaseous products has been described (5).

Analysis of Liquid Products:

The amounts of liquid products obtained in the runs were of the order of 1-2 milligrams. These amounts were so small that no chemical tests of the liquid products were attempted. It is probable that the isolation of liquid products by the method used was not complete, for theoretically 6-7 milligrams should have been formed in certain runs. The reason for this discrepancy is not known.

GAS ANALYSIS

Gas analyses of the products of the runs were carried out using a system of micro analysis designed originally by Blacet and Leighton and described by them and their coworkers in a number of papers (18) (19). In this work the gases tested for, were - in order -:

carbon dioxide

ethylene and other unsaturated hydrocarbons

carbon monoxide

hydrogen

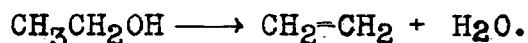
methane and ethane

Because of the importance of reliable gas analysis in this investigation, the reagents and procedures for each gas were tested against specially prepared samples with known proportions of the particular gas. Reagents and procedure for oxygen were tested also. The results of these investigations are given below.

Carbon Dioxide: (18) The reagent was potassium hydroxide fused in a platinum loop and exposed to the air until it had picked up a film of moisture. This reagent was tested against mixtures of carbon dioxide (obtained from "dry ice") and air. If properly prepared the reagent gave accurate and reproducible results, with complete absorption of carbon dioxide in five minutes or less. The bead had to appear wet and shiny, however;

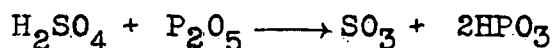
otherwise absorption was slow.

Ethylene and Unsaturated Compounds: (19) The reagent was fuming sulphuric acid introduced in a sintered glass bead, and followed by a fused potassium hydroxide bead. It was very difficult to get accurate results with this reagent because of the difficulty with which absorption of the ethylene takes place. The reagent was tested against air-ethylene mixtures. The ethylene was prepared from ethanol and sulphuric acid (16) according to the reaction:



Commercial fuming sulphuric containing 15 percent sulphur trioxide was tried first and found to give consistently low results. Sulphuric acid activated with nickel and silver sulphates (14) and 15 percent fuming sulphuric containing nickel and silver sulphates were then tried and both found unsatisfactory. Warming of the gas holder likewise was ineffective.

Finally sulphur trioxide was prepared and used to make a 30 percent fuming sulphuric acid mixture which proved more satisfactory. The sulphur trioxide was prepared by heating a mixture of sulphuric acid and phosphorous pentoxide according to the reaction:

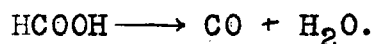


Tepid water was run through the condenser while the

sulphur trioxide was distilling over to prevent polymerization and plugging of the condenser. The 30 percent sulphur trioxide mixture was stored in a tight glass-stoppered bottle and sealed with parawax.

In using this reagent the bead was dipped slowly into a fresh portion, taken out and touched once to the side of the container to remove some of the excess acid; then inserted swiftly into the holder, where it could be seen to fume. After two minutes it was removed and one or more potassium hydroxide beads inserted to take up the sulphur trioxide vapour and the excess acid floating on the mercury. The whole procedure was then repeated one or more times until there was no further reduction in volume. For best results the sintered glass bead was cleaned in hot cleaning solution, washed, and dried before each determination. The determination of ethylene is fairly reliable when carried out with these precautions.

Carbon Monoxide: The reagent used was compressed silver oxide (19). This reagent was tested against carbon monoxide prepared by dropping formic acid into concentrated sulphuric acid at 100° C according to the reaction:



This method is satisfactory as far as the determination of the carbon monoxide itself is concerned if:

- (1) a large piece of silver oxide (at least 2mm.

square) is used.

(2) the silver oxide has freshly fractured surfaces

(3) adsorption is allowed to take place for 15 minutes. The reagent takes up the gas slowly but adsorption is substantially complete in this time.

The reagent should not, however, be allowed to remain in contact with the gas mixture for longer than 15 minutes because it adsorbs hydrogen as well as carbon monoxide. A silver oxide bead placed in pure hydrogen picked up 3 percent of the total volume in 15 minutes. Table II gives results showing the error in carbon monoxide determination produced by the presence of hydrogen.

TABLE II

Adsorption of H_2 by Ag_2O

Original mixture		Vol. taken up by
Vol. H_2	Vol. CO	Ag_2O in 15 minutes
1. .0841	.0183	.0204
2. .0532	.0479	.0485
3. .0072	.0863	.0865

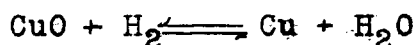
The method is thus fairly accurate for the determination of large quantities of carbon monoxide in the presence of small quantities of hydrogen, which was all that was required in this investigation.

Hydrogen: Hydrogen was determined by heating with a combined bead of cupric oxide and potassium hydroxide (20,22). Hydrogen for testing the reagent was prepared from dilute HCl, zinc, and CuSO₄ catalyst. Both the preparation of the bead and the amount of heating were important in obtaining accurate and reproducible results. After a great deal of trial and error the following procedure was adopted:

A slurry of powdered cupric oxide and 6N potassium hydroxide was mixed and dried. A small piece of the resulting black mass was fused into a platinum loop in an oxygen flame, and, while still molten, was touched to a smaller piece of potassium hydroxide. The bead was heated over a hot-plate and touched on one side only to powdered cupric oxide; then heated again to smooth out the rough cupric oxide surface. The resulting bead had both an effective cupric oxide and an effective potassium surface and did not melt away from the loop upon heating. The bead was placed in position on the centre axis of the gas holder and the glass rod wedged into the guide with a sliver of wood so that the bead did not touch the glass at any point. The heater, top compartment filled with lead, was attached so that it sat as low as possible over the gas holder, and was connected to a variac. The variac was set at 20 volts for one minute and at 16-17 volts for 9 minutes. Then the heater was quickly removed and the gas mixture allowed to cool for 2-3 minutes

before removing the bead.

The temperature and time of heating must be sufficient to reduce the hydrogen, but must not fuse the potassium hydroxide to any extent. If the potassium hydroxide is fused the concentration of water vapour is apparently increased and the equilibrium,



is shifted to the left. In every trial where fusion of the potassium hydroxide took place, only 70 to 90 percent of the hydrogen was reduced. Besides this disadvantage the fused potassium hydroxide tends to coat the inside of the gas holder and thus trap out some of the gas mixture. Very accurate results can be obtained, however, using the method outlined above.

Methane and Ethane: (21, 22) These gases are analysed by combustion and subsequent measurement of the volume of carbon dioxide formed. They can be determined together since ethane causes a reduction of 5/2 times its volume on combustion, forming two volumes of carbon dioxide; whereas methane causes a reduction of twice its volume, forming an equal volume of carbon dioxide.

The technique used was similar to that described by Turner (5). The only modification was to place a 30 ohm resistance and a variac in the circuit with the combustion filament. With this circuit the temperature of the

filament could be controlled very smoothly and it burnt out much less frequently.

The analysis of methane by itself, uncomplicated by the presence of any ethane, was found to be fairly accurate if:

- (1) The gas holder was thoroughly clean.
- (2) The temperature of the platinum filament was raised slowly so as not to explode and char the mixture.
- (3) The temperature was not raised above the point where the filament had a red-orange color.

The simultaneous analysis of methane and ethane, however, seemed to require a higher temperature and longer heating. This apparently caused oxidation of material other than the gases and produced very erratic results. The cause of this trouble was not investigated. Percentage ethane and methane was determined for some of the runs. These results, however, are of a lower order of accuracy than the results for the other constituents.

Oxygen: (18) The reagent used was yellow phosphorous fused into a platinum loop. The reagent would not take up the oxygen until any water vapor present had first been removed with a phosphorous pentoxide bead. The yellow phosphorous either removed the oxygen completely or did not act at all. If the reaction was

taking place properly, a fuming of the reagent could be seen.

In general, reliable results for a gas sample could be obtained only by making at least two, and usually more, complete analyses which checked. A single analysis was found to be completely unreliable.

It was found very important to keep the capillary and the mercury clean. The mercury was best cleaned by filtering through a dry filter paper with a hole pricked in the bottom. The capillary was generally cleaned by clamping it in upright position, immersing the tip in hot cleaning solution, and pulling the solution down through the capillary with suction, followed by distilled water, alcohol, and ether in that order. In some cases when cleaning solution seemed ineffective, hot concentrated sodium carbonate solution proved more efficient.

Summary of Runs:

A number of runs were made at 400°, 450°, and 550°C. At each temperature two complete runs were carried out - one with a measured pressure (about 30cm.) of methane and a weighed amount of dimethyl acetal; the second under the same conditions but with dimethyl acetal alone, at approximately the same partial pressure. By this means it was hoped to cancel out the course of the dimethyl acetal decomposition in which unsaturates were produced,

and to determine whether unsaturateds were formed from decomposition of the methane itself. Besides these six runs, a number of others were made for special purposes; all are listed below:

Run #1: Methane and dimethyl acetal at 400°C for five hours.

Run #2: Dimethyl acetal alone at 400°C for five hours.

Run #3: Methane and dimethyl acetal at 450°C for five hours.

Run #4: Dimethyl acetal alone at 450°C for five hours.

Run #5: Methane and dimethyl acetal at 550°C for two hours.

Run #6: Dimethyl acetal alone at 550°C for two hours.

Run #7: Methane and dimethyl acetal at 550°C for one minute.

Run #8: Dimethyl acetal alone at 550°C for one minute.

Run #9: Methane and dimethyl acetal (0.0017gm) at 550°C for one hour.

Run #10: This run was made to determine the amount of liquid products after reaction of methane and dimethyl acetal at 550°C for one hour. After one hour the pressure was recorded, the furnace turned off and left overnight to cool,

and removed the next morning. Then a rubber container, made from a section of inner tube, was wired around the base of the reaction chamber, so that the chamber was surrounded by a water-tight jacket. This was filled with a cooling mixture made by freezing a saturated solution of sodium chloride in the refrigerator. The cooling of the reaction chamber reduced the vapor pressure of possible liquid products to a negligible quantity, so that the pressure exerted would be only that of the permanent gases. The lowest pressure as shown by the manometer was recorded together with the temperature of the freezing mixture.

Run #11: This run was similar to run #10 but with dimethyl acetal alone.

The next chapter contains the analysis of data obtained from these runs.

IV. TREATMENT OF DATA:

Pressure-Time Curves:

The data obtained from the reaction rate measurements of runs 1-6 were plotted, as shown in graphs I, II and III. The curves were plotted in pairs for each temperature, one representing the decomposition of methane and acetal, and the other the decomposition of the acetal alone. The initial pressure of the methane was subtracted from all the pressure readings of the acetal-plus-methane curve; and the resulting pressures multiplied by the ratio of the two weights of acetal used. The two curves could then be directly compared and any differences between them must have been caused by reaction between the acetal and the methane. The initial pressures of the acetal were calculated and are shown on the graphs.

The graphs seem to show that there is not much reaction between the methane and acetal for they are very similar in shape. The $t_{\frac{1}{4}}$ and $t_{\frac{1}{2}}$ values for 400°C and 450°C as shown in Table III seem to indicate that the initial split of the acetal is slightly retarded and the secondary decomposition slightly accelerated by the presence of the methane, but the effects are very slight. At 550°C both the curves show a pronounced decrease in pressure after two minutes, continuing for about fifteen minutes before the pressure again begins to rise.

TABLE III.

SUMMARY OF RUNS

<u>Run</u>	<u>Temp.</u> °C	<u>Time</u>	<u>Wt.Acetal</u> gms	<u>P_i</u> <u>Acetal</u>	<u>P_i</u> <u>CH₄</u>	<u>P_f</u>	$\frac{P_f - P_i(\text{CH}_4)}{P_i(\text{acetal})}$	$\frac{P_f}{P_i(\text{acetal})}$	<u>t_{1/4}</u> min.	<u>t_{1/8}</u> min.	<u>Wt.Liquid</u> <u>Product</u> gms
1	400	5 hrs	.0217	5.88	32.00	50.30	3.12	-	0.5	7	.0005
2	400	5 "	.0217	5.88	-	18.20	-	3.10	0.4	7.5	.0007
3	450	5"	.0221	6.43	33.65	57.40	3.69	-	0.3	1.5	.0010
4	450	5 "	.0228	6.64	-	24.20	-	3.65	0.2	2.3	.0014
5	550	2 "	0.0176	5.86	34.20	60.80	4.53	-	-	0.1	.0010
6	550	2 "	.0235	7.83	-	35.15	-	4.48	-	0.1	.0008
7	550	1 min	.0258	8.61	28.70	-	-	-	-	-	.0027
8	550	1 "	.0315	10.50	-	-	-	-	-	-	.0037
9	550	1 hr	.0017	0.57	30.35	34.85	-	-	-	-	-
10	550	1 "	.0190	6.30	28.95	56.45	4.38	-	-	-	-
11	550	1 "	.0446	14.80	-	69.75	-	4.72	-	-	-

This effect must be due to polymerization of some of the products, but just what compounds are involved is uncertain.

In Table III are tabulated observed initial pressures of methane, calculated initial pressures of acetal, and observed final pressures, for all the runs in which pressure readings were taken. If the initial pressure of methane is subtracted from the final pressure for a methane-plus-acetal run the ratio $\frac{P_f - P_1 (\text{CH}_4)}{P_1 (\text{acetal})}$ may be calculated.

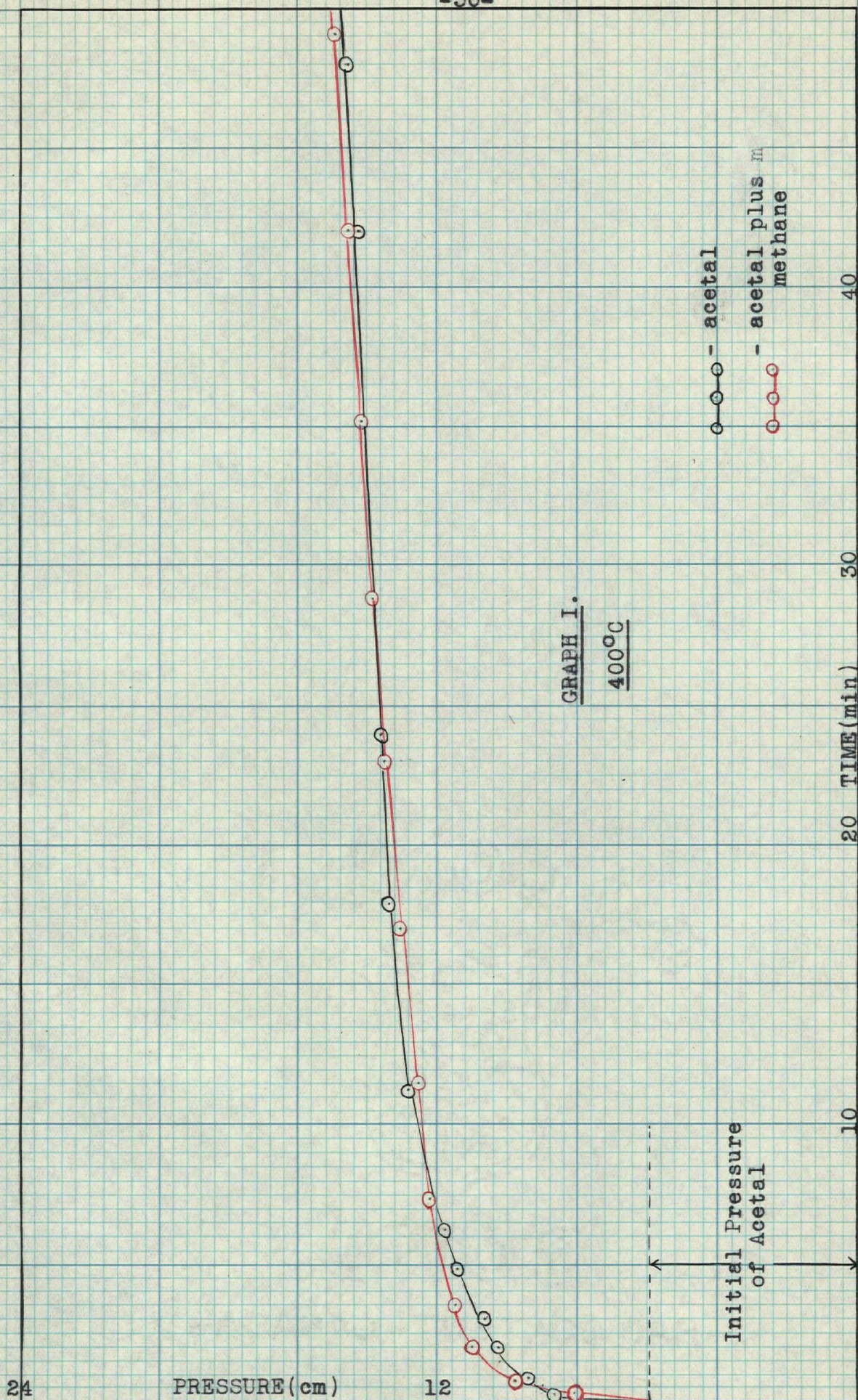
The comparison of this ratio with $\frac{P_f}{P_1 (\text{acetal})}$ for the run with acetal alone at the same temperature might give some indication of the decomposition of the methane. At 400° and 450°C the ratios are the same within the limits of the experimental error. At 550°C the ratios are the same for runs 5 and 6, in which the reactants were heated for two hours. In runs 10 and 11, however, which were made to investigate the percentage of liquid products formed at 550°C the ratio $\frac{P_f - P_1 (\text{CH}_4)}{P_1 (\text{acetal})}$ is substantial-

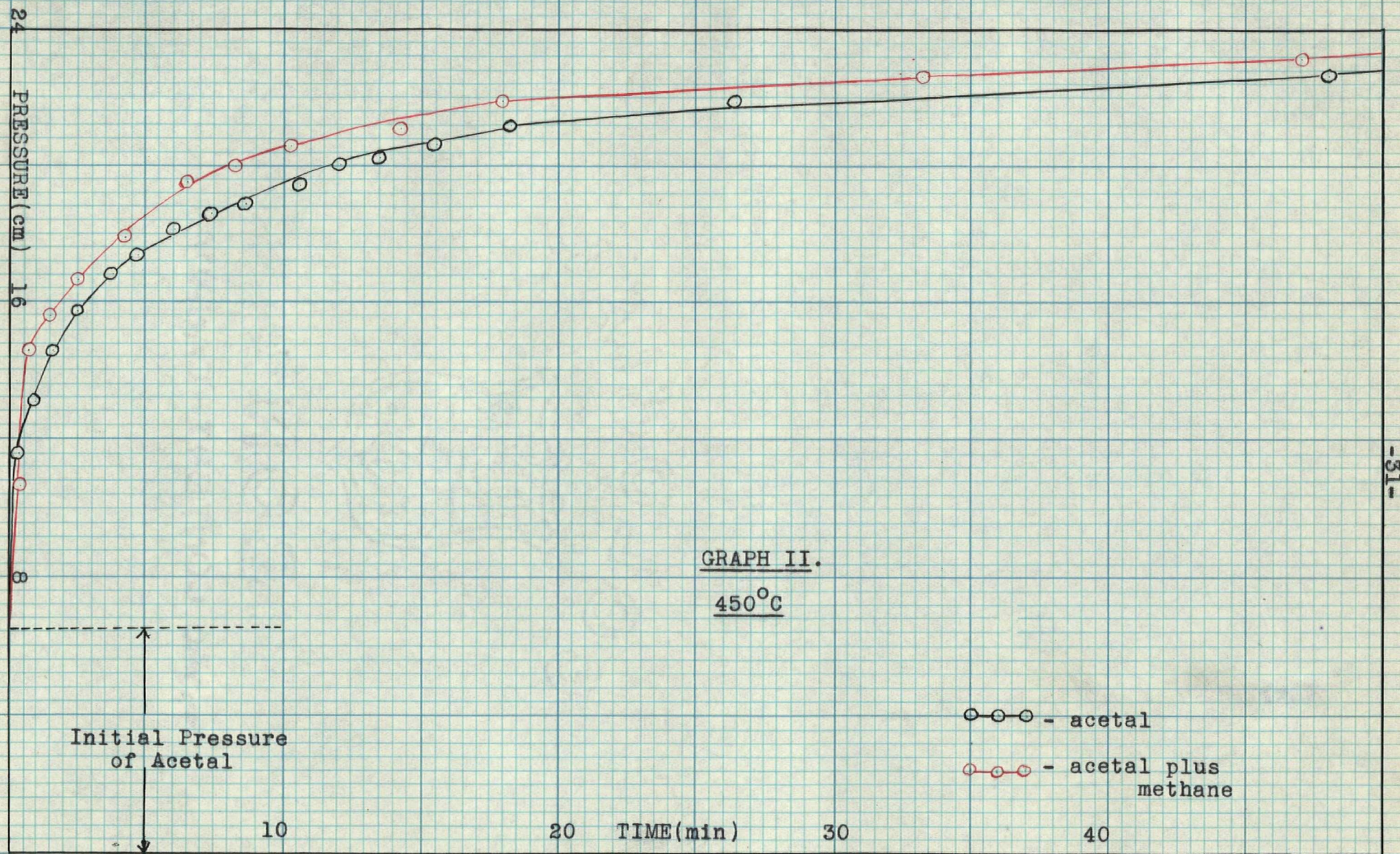
ly lower than $\frac{P_f}{P_1}$ for the acetal alone. The reactants

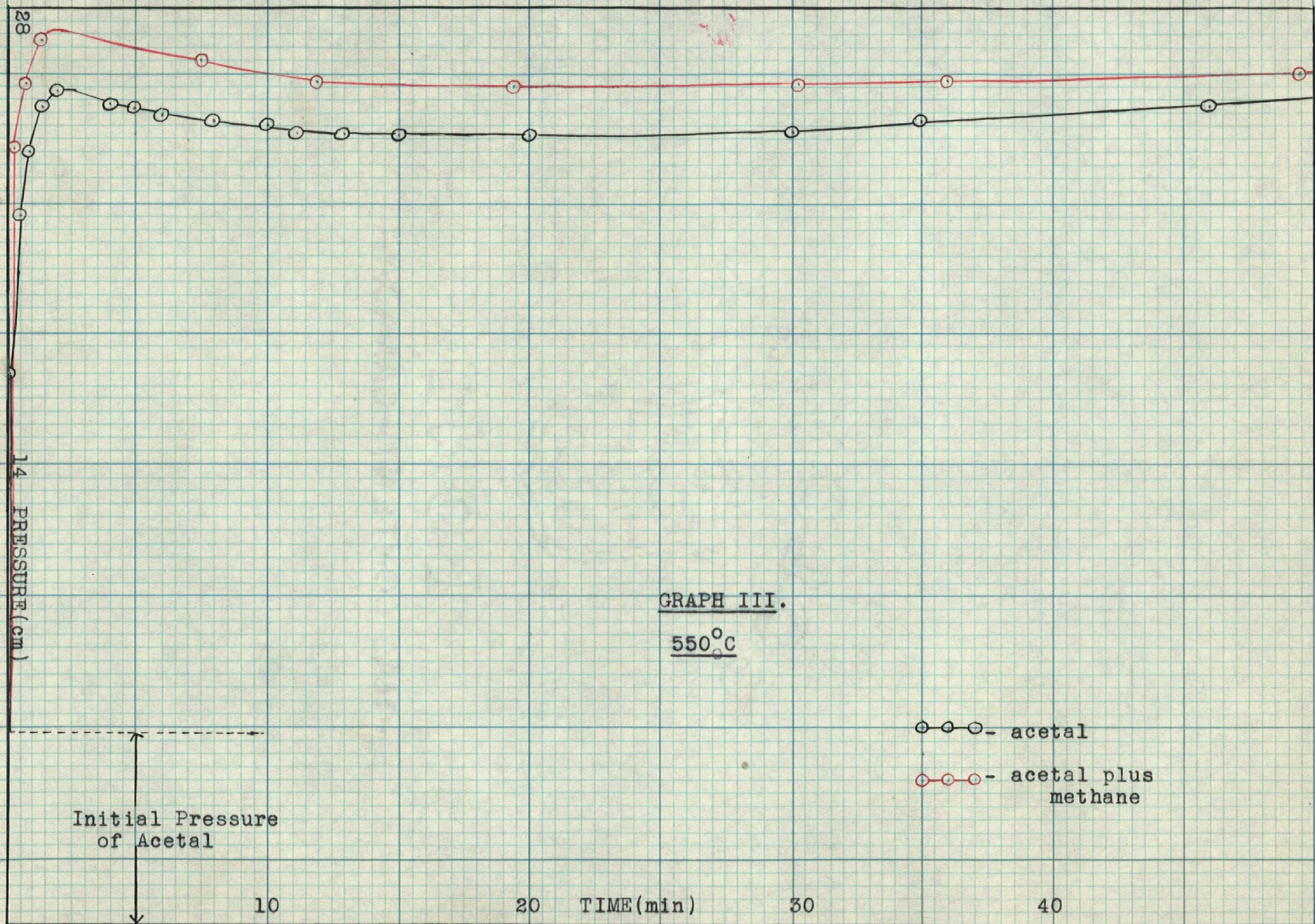
were heated for one hour at 550°C in this case. The difference may indicate a reduction in pressure of the methane by decomposition and formation of longer chain

250

-30-







compounds, or it may be that the surface conditions were different. For at the conclusion of run 10 the reaction chamber was strongly cooled with a freezing mixture, and there might have been small amounts of material adsorbed on the walls and not removed by pumping, which increased the extent of the acetal decomposition in run 11.

Gas Analyses:

Decomposition of the dimethyl acetal produced ethylene and hydrogen, which were the expected products if decomposition of the methane occurred. For that reason it was necessary to analyse the decomposition products of the acetal by itself to obtain information about the methane. Gas analyses were carried out for all runs except 10 and 11, and the results were tabulated (Table IV).

Since the methane diluted the concentrations of the other constituents when it was included in a run, a method of comparison was necessary. This was complicated by the uncertain amounts of liquid products formed at the lower temperatures and frozen out in the trap. In dealing with the acetal-methane run at 400°C (run 1) it was assumed that one third of the final pressure of the dimethyl acetal was due to liquid products. The percentage of the constituents found in the gas analyses were multiplied by the factor
$$\frac{P_1 (\text{CH}_4)}{2/3(P_f - P_1 (\text{CH}_4))}$$

TABLE IV.RESULTS OF GAS ANALYSES

<u>Run</u>	<u>Temp.</u> <u>°C</u>	<u>Time</u>	<u>%CO₂</u>	<u>%C₂H₄</u>	<u>%CO</u>	<u>%H₂</u>	<u>%CH₄</u>	<u>%C₂H₆</u>
1	400	5 hrs	0.8(2.8)	4.6(16.1)	12.2(42.7)	1.1(3.8)	-	-
2	400	5 "	4.3	10.6	37.7	2.8	-	-
3	450	5 "	0.5(1.5)	1.9(5.7)	16.8(50.4)	2.1(6.3)	-	-
4	450	5 "	0.6	5.7	41.8	6.9	-	-
5	550	2 "	0.5(1.2)	3.3(7.5)	20.2(46.0)	5.9(13.5)	42.6	17.5
6	550	2 "	1.3	1.6	40.0	12.3	6.0	39.0
7	550	1 min	0.5(0.9)	2.7(4.7)	17.8(31.0)	4.7(8.2)	-	-
8	550	1 "	2.1	2.2	38.0	11.1	-	-
9	550	1 hr	0.3(3.9)	0.7(9.0)	3.5 (45)	0.9(12.0)	-	-

These "comparative" percentages are given in Table IV in parentheses after the true percentage obtained in the actual analysis. Using the adjusted figures, the percentages of constituents of run 1 can be directly compared with the percentages occurring in run 2. The percentages of the constituents in run 3 were multiplied

by the factor
$$\frac{P_1 (\text{CH}_4)}{5/7 (P_f - P_1 (\text{CH}_4))}$$
 for comparison with

percentages in run 4. At 550°C it was assumed that no liquid products were formed. Thus the percentages of constituents in runs 5, 7, and 9 were multiplied by the factor
$$\frac{P_1 (\text{CH}_4)}{P_f - P_1 (\text{CH}_4)}$$

The "adjusted" percentages for runs 3, 5, 7, and 9 are given in parentheses. They are directly comparable to the percentages of the various constituents at the same temperatures for the acetal alone.

At 400 and 450°C the differences in amounts of ethylene or other constituents caused by the presence of the methane are not significant, when we consider the crudity of the method of comparison. At 550°C, however, there is a definite increase in the amount of ethylene when methane is present, although the total amount is still small. This increase is present in runs 5, 7, and 9. Its significance will be discussed in a later paragraph.

Factors Involved:

Effect of Temperature: At 400 and 450°C no significant differences in amounts of ethylene were caused by the presence of the methane. Since the relative amounts of ethylene from the dimethyl acetal were highest at the lower temperatures, however, comparison is very unsatisfactory. The presence of methane caused a definite increase in the amounts of ethylene at 550°C.

Effect of Period of Heating: Runs 7 and 8 were made to study the effect of a short reaction time (one minute) at 550°C. Analysis of the gaseous products showed some differences between the results and results at 550°C with two hours heating. They are not large enough for the drawing of any conclusions, however, and may not be significant.

Effect of Diminishing the Amount of Acetal: In run 9, 0.0017 grams of acetal was heated with about 30cm. of methane for an hour at 550°C. Adjusting the figures for the gas analysis in the usual way gave results which were not significantly different from run 5. A tentative conclusion is that the amount of ethylene produced is dependent on the amount of acetal.

Ethylene from the Dimethyl Acetal: Both of the mechanisms suggested by Turner (5) for the decomposition of the acetal involve the formation of large quantities

of ethylene. Since the amounts of the gas found in the decomposition products are relatively small, Turner postulated the polymerization of the ethylene. The following experiment seems to cast some doubt upon the formation ethylene in any quantity at 550°C.

Runs 10 and 11 were made to determine what fraction of the products of decomposition at 550°C were liquids. Pressure readings were taken after one hour at 550°C and then later at -19°C. The pressure at 550°C reduced to terms of -19°C should give the pressure at -19°C if the decomposition products are all gases at that temperature. Dividing this figure into the actual pressure at -19°C should give the fraction of permanent gases in the mixture. The actual results obtained are shown in Table V.

TABLE V.

Run	$P_{550^{\circ}}$ cm.	$P_{550^{\circ}} \times \frac{254}{823}$ cm.	$P_{-19^{\circ}}$ cm.
10	56.45	17.45	17.90
11	69.75	21.55	22.6

It will be noted that $P_{-19^{\circ}}$ is slightly greater, not less, than the reduced value of $P_{550^{\circ}}$ for both runs. This is probably due to further decomposition over the hours the furnace was cooling. The conclusion to be drawn is that there are no liquid products formed when

the acetal decomposes at 550°C. But what then happens to the ethylene? It might combine with hydrogen to form ethane, but this seems unlikely as the percentage of hydrogen in the decomposition products increases with increasing temperature. The ethylene might form a polymer, with negligible vapor pressure, on the walls of the reaction chamber, but this also is unlikely considering the high value of P_f at 550°C. Thus it seems that P_i ethylene was formed in only small quantities. Harris (12) proposed a mechanism for the decomposition of methyl vinyl ether in which ethylene did not appear. His theory seems to fit the facts better at higher temperatures than does Turner's.

If the factor of the polymerization of ethylene need not be considered, it seems that the small proportion of ethylene found in run 6 is in fact the total ethylene formed at this temperature. Methane, acting merely as an inert diluent of the dimethyl acetal vapor, would not be likely to change the course of the dimethyl acetal decomposition. Thus the increase in amount of ethylene produced by the presence of the methane may be evidence for the decomposition of the methane.

This conclusion is speculative, however, and much further work must be done before any satisfactory conclusions can be drawn. The decomposition of the dimethyl

acetal is complex and is affected by surface conditions and other factors. The uncertainty of the exact mechanism makes the effects of this decomposition on that of the methane difficult to interpret.

Summary:

- (1) The heating of methane with dimethyl acetal at 550°C caused an increase in the proportion of ethylene over that found in the decomposition of dimethyl acetal alone. This was not conclusive evidence that decomposition of the methane had taken place, because of the complexity of the factors entering into the dimethyl acetal decomposition.
- (2) This effect was not apparent at 400° and at 450°C, but it could not be accurately studied because of the larger amounts of ethylene formed by the acetal decomposition at these temperatures.
- (3) At 550°C the increase in amount of ethylene is largely independent of time of heating.

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