QUANTITATIVE ANALYSIS OF COMBUSTION PRODUCTS BY GAS CHROMATOGRAPHY

THE OXIDATION OF A RICH n-PENTANE–AIR MIXTURE IN A FLOW SYSTEM[1]

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ABSTRACT

A description is given of an apparatus suitable for investigations of the oxidation and decomposition reactions of volatile hydrocarbon vapors in a flow system. Most of the reaction products are analyzed quantitatively by gas chromatography in a single-stage process involving a simple column-temperature programming technique. The products of the oxidation of a rich mixture of n-pentane and air in an annular reactor of Vycor over a wide temperature range are shown in detailed analysis. The products, as identified by several techniques including time-of-flight mass spectrometry and infrared spectrophotometry, include C_2—C_5 mono-olefins, two di-olefins, C_1—C_4 saturated aldehydes, an unsaturated aldehyde, and 2-methyl tetrahydrofuran in addition to those usually associated with the complete oxidation of n-pentane.

INTRODUCTION

Earlier studies in this laboratory of the low-temperature oxidation of n-pentane (1, 2) indicated the need for an efficient means of analyzing the complex mixture of products so obtained. It was possible to determine the effect of certain variables on the total concentration of any particular class of components, but this information was insufficient for the determination of a reaction mechanism. The analytical difficulty is largely responsible for the lack of quantitative information concerning the effect of temperature and other variables on the mechanism of the oxidation of hydrocarbons.

One of the first attempts at a detailed analysis was that of Ubbelohde (3), who identified some of the liquid oxidation products of pentane after fractional distillation, using ultraviolet spectroscopy and chemical methods. With the development of liquid partition chromatography and polarography more of the products could be analyzed, as demonstrated by Malmberg and others (4, 5), but the experimental method was complicated and the results were of limited quantitative value.

Detailed analyses of complex mixtures of combustion products can now be effected by using the newly developed gas chromatographic techniques. Thus Yokley and Ferguson (6) were able to investigate qualitatively some of the products of the cool flame combustion of propane; Kyryacos, Menapace, and Boord (7) determined the identity of many of the components of the cool flame combustion products of n-hexane, and Hughes, Hurn, and Edwards (8) separated and identified oxygenated hydrocarbons in automotive engine combustion products using a three-stage unit.

Gas chromatography was used in earlier work by the authors to separate liquid oxidation products, in conjunction with Orsat analysis of the normally gaseous products. The liquid products were collected in traps surrounded by dry ice – acetone and ice–water mixtures and the condensates had to be transferred by micrometer syringe to the chromatographic column. This procedure entailed large sources of error in the handling of the samples and volatilization of some of the components. In addition, calculation of selectivities (i.e. moles of product formed/mole of fuel consumed) was tedious because it was necessary to combine the analyses of the two condensates. In addition, the calculations

involved the assumptions of uniformity of the flow rate and the furnace temperature, which were shown to be variable over the long period required for sampling.

The present development of a reproducible sampling method allowed this technique to be extended to a more detailed study of the influence of temperature on the oxidation of an n-pentane – air mixture.

APPARATUS

General Description

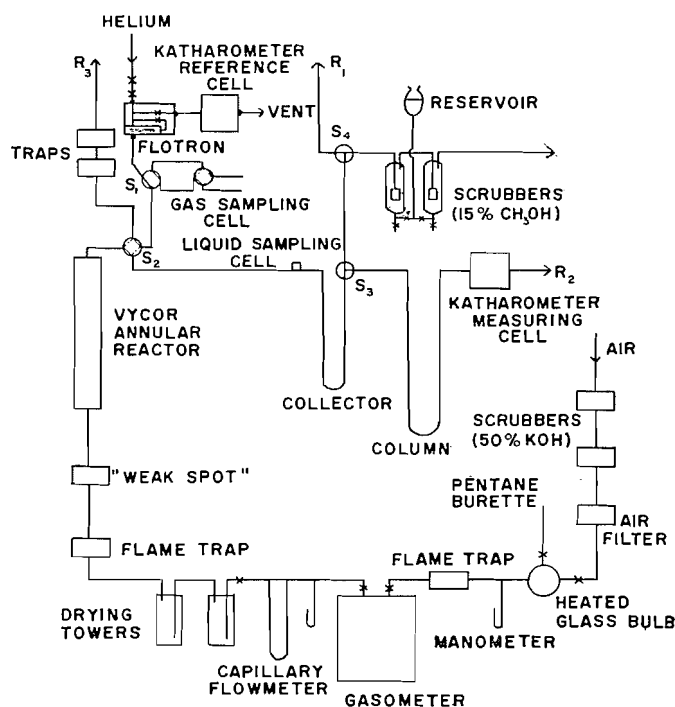The apparatus is shown diagrammatically in Fig. 1. The required mixture of carbon-

FIG. 1.   Schematic diagram of apparatus.

dioxide-free air and n-pentane was prepared and stored in the gasometer. From this vessel it was passed at a known rate of flow through the reactor, which, for this study, was constructed of Vycor glass and was annular in form. The reactor dimensions and its positioning in a tubular furnace have already been described (2).

Until steady-state conditions were fully established so that a sample could be taken for analysis, the oxidized mixture was allowed to flow from the reactor through ice–water and dry ice – acetone cooled condenser traps to vent at the rotameter, R_3.

During this period, the eluent gas (helium) was passed through reducing valves to the Burrell "Flotron". This is a device for maintaining a reproducible volume flow and splitting the eluent stream to allow a small flow through the katharometer reference cell of the modified Burrell K1 Kromotog which was used for the analysis of the condensable oxidation products. The eluent was allowed to bypass the gas sampling cell at S_1 and pass through the collector, the column, and the katharometer measuring cell to vent at the rotameter, R_2.

Sampling for Chromatographic Analysis

In taking a condensable product sample for chromatographic analysis the flow streams

were redirected so that helium passed through S_2 and the traps to vent at R_3 while the reactor effluent was passed during a measured time interval (usually 5 minutes) through the liquid-air-cooled collector and three-way stopcocks S_3 and S_4 to vent at rotameter R_1. The collector was a U tube with a side-arm joined to it by a three-way stopcock. It was wound with resistance tape and contained glass wool and a small amount of crushed firebrick to prevent minute crystals of condensate from being blown through it.

To complete the sampling, four-way stopcock S_2 was turned to allow eluent gas to sweep the sample remaining in the lines into the collector. Then stopcock S_3 was turned so that eluent flowed through the column. Finally, the liquid-air bath was removed and the sample in the collector was volatilized into the helium stream proceeding to the column by heating the collector for 4 minutes at about 150° C.

The uncondensed gases emerging at R_1 during the early stages of the above sampling procedure were sampled by microsyringe from the exit line leading to R_1. This sample was transferred to a homemade chromatographic unit with a Veco thermistor detector cell for analysis on an adsorption column.

The Column Material and Analysis Technique

The separation of the compounds condensed from the reactor effluent was effected on an 8-ft column packed with 25% w/w bis[2-(2-methoxyethoxy)ethyl] ether (MEEE) on 30–60 mesh C-22 firebrick. This substrate was selected as a result of a series of comparison tests using 11 different stationary phases. The operating details for these tests and a comparison of the effectiveness of these substrates for various separations are given in Table I. Subsequently it was observed that the same choice of optimum stationary phase had been made by Yokley and Ferguson (6). Chromatograms of the separations

TABLE I

Comparison of various stationary phases

Stationary phase 25% w/w on 30–60 mesh C-22 firebrick	Maximum usable temp., °C	Ethylene and carbon dioxide separation	*cis* and *trans* 2-Pentene separation	Hydrocarbon peaks	Aldehyde peaks	Water peak	Remarks
β,β'-Oxydipropionitrile	100	P	P	P	E	F	Unusual order of elution
Acetonyl acetone	20	E	F	E	F	P	Baseline unstable
Dimethyl sulpholane	40	F	P	E	E	E	Unstable at higher temp. otherwise good
Triethanolamine	40	P	P	P	F	P	No peaks beyond acetaldehyde
Acetoacetic ester	40	E	F	F	P	P	Water strongly held
Ethylene glycol monoethyl ether	40	P	P	F	P	P	No peaks beyond pentenes
Triacetin	80	P	P	F	E	E	Good for higher temp. separations
Bis(2-methoxyethyl) phthalate	100	P	P	E	E	E	Good for higher temp. separations
Bis[2-(2-methoxyethoxy)ethyl] ether	70	E	F	E	E	E	Best stationary phase tested
Dinonyl phthalate	130	P	P	F	F	F	Unusual order of elution
Carbowax 20M	225	P	P	E	E	E	Tested at 60° C; ineffective at 40° C

NOTE: E = excellent, F = fair, P = poor or not observable. Column details: eluent, helium at 50 cc/minute; sample, oxidation products of 54 μl of *n*-pentane. Column temperature, 40° C.

effected by two of the poorer substrates are shown in Fig. 2. Compounds corresponding
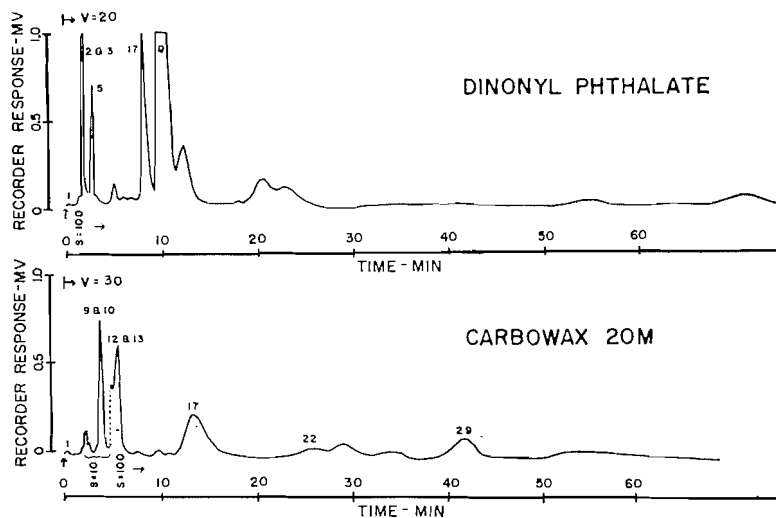to the various peak numbers are listed in Table II. These chromatograms afford yet

FIG. 2.   Comparison of the separations on different substrates.

TABLE II

Identification of products shown in chromatograms

Peak No.	Compound	R.R.T. standards	R.R.T. products	Method of identification		
				M	I	R.R.T.
1	Air	0.00	0.00			x
2	Ethylene	0.06	0.06	x		x
3	Carbon dioxide	0.10	0.10	x		x
4	Unknown		0.18			
5	Propylene	0.18	0.19	x		x
5A	Unknown		0.34			
6	1-Butene	0.46	0.49	x_p		x
7	trans-2-Butene	0.58	0.61	x_p		x
8	cis-2-Butene	0.70	0.72	x_p		x
8A	Unknown		0.95			
9	n-Pentane	1.00	1.00	x	x	x
10	1-Pentene	1.30	1.29	x		x
12	trans-2-Pentene		1.57	x_p		x
13	cis-2-Pentene		1.60	x_p		x
16	Cyclopentane	2.3	2.4	x		x
17	Acetaldehyde	2.7	2.6	x	x	x
18	1,3-Pentadiene		2.9	x_p		
19	1,4-Pentadiene		3.1	x_p		
20, 21	Unknown		3.4			
22	Propionaldehyde	4.3	4.2	x	x	x
23	Acetone	4.7	4.6	x	x	x
24	Acrolein		5.0	x		
25, 26	Methyl alcohol		5.3	x	x	
27	Unknown		5.5			
28	Unknown		5.9			
29	2-Methyl tetrahydrofuran	6.6	6.4	x	x	x
30	n-Butyraldehyde	6.5(?)	7.0	x		x_p
31	Unknown		7.4			
31A	Unknown		8.0			
32, 33	Water	8.8	9.0			x

NOTE: R.R.T. = Relative retention time, n-pentane = 1.00 on 25% w/w bis[2-(2-methoxyethoxy)ethyl] ether and 30–60 mesh
          C-22 firebrick column at 25° C.
   M = Mass spectrometry.
   I = Infrared spectroscopy.
   x = Identified, x_p = tentatively identified.

another example of the remarkable versatility of the gas–liquid chromatographic technique. Thus, the order of elution of the polar compound, acetaldehyde (peak 17), relative to the non-polar n-pentane (peak 9), can be radically altered, as shown, by suitable choice of stationary phase polarity.

The following very simple but quite effective system of column-temperature programming was used to obtain a reasonably efficient separation of the condensed sample in a single operation. The column temperature at the beginning and for the first 10 minutes of each analysis was 25° C. At the end of this period an electric current at a potential of 30 volts was passed through the resistance wire wound on the column. The rate of increase of temperature was such that a temperature of 60° C was attained in another 15 minutes. A fixed eluent flow rate of 100 ml per minute (25° C and 760 mm Hg), as measured at the downstream end of the chromatograph, was always maintained by the "Flotron". Hence there was little or no change in the base line due to the temperature change.

With the MEEE substrate a low initial temperature was ideal for the separation of carbon dioxide and the lower olefins. On the other hand, the gradually increasing temperatures in the following period prevented excessive peak broadening of the higher boiling components without seriously impairing their separation. The temperature finally attained allowed the analyses to be completed in less than 1 hour. A representative chromatogram obtained in this manner from a 5-minute sample of the reactor effluent taken when the maximum wall temperature was 509° C is given in Fig. 3. The excellent
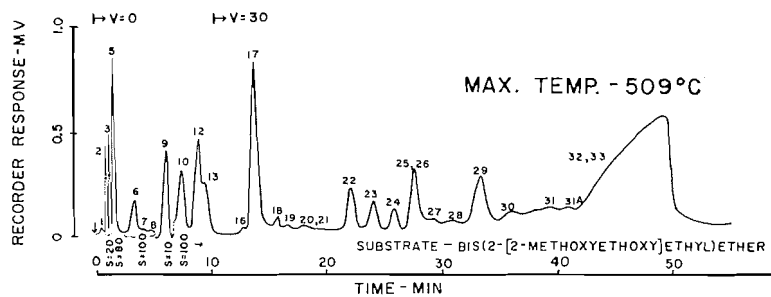

FIG. 3.   Representative oxidation product chromatogram.

separation of most of the constituents and the stability of the base line despite the relatively large change in column temperature are readily apparent.

A further temperature increase to 90° C would have permitted the analysis of part of the organic acid content of the sample. However, a noticeable "bleeding" of the substrate occurs at this temperature. Hence, the analysis for the acid content was performed on a separate sample by a titration method.

The uncondensed gases were separated on a 15-ft column of 30–60 mesh 5A Linde molecular sieves. This material was dried for 6 hours in a nitrogen stream at a temperature of 300° C prior to packing. Hydrogen, oxygen, nitrogen, methane, and carbon monoxide were readily separated and all but the hydrogen were quantitatively determined on this column at a temperature of 100° C with helium flowing at 50 ml per minute. With this eluent, the sensitivity for hydrogen was about 1/20th of that for the other gases due to the similarity of its thermal conductivity to that of helium. Hence quantitative results for this gas were not obtained unless its concentration exceeded about 1% by volume of the uncondensables.

Formaldehyde Analysis

Initially, it was hoped to measure formaldehyde by gas chromatography. However, a number of experiments showed that polymerization of formaldehyde at low temperatures would require the use of a column temperature exceeding 100° C and controlled within fine limits. At these elevated temperatures a formaldehyde peak was observed. However, other oxidation products which could not be resolved interfered and a quantitative determination could not be made. In addition the substrate "bleeding" mentioned earlier became appreciable at temperatures above 100° C and the useful life of the column was thereby excessively reduced. Work on a gas chromatographic separation of formaldehyde is continuing.

The polarographic methods for formaldehyde could not be applied because of the mixture complexity and especially because of the presence of acrolein, which interferes. Hence, a chemical method of analysis was indicated. Since a large number of analyses was projected the specific reaction with chromotropic acid as recommended by West and Sen (9) was adopted rather than the precipitation and separation of derivatives.

The sample was collected prior to the one for gas chromatographic analysis by a precisely similar technique. This was transferred to and absorbed in scrubbers containing 15% methyl alcohol. An aliquot of this solution was treated with chromotropic acid in sulphuric acid solution. After the mixture was heated in a boiling water bath for 5 minutes to develop the color, the color maximum at 560 mμ was read and compared with that of a similarly treated standard formaldehyde solution.

Acid Analysis

The sampling technique was modified by (a) condensing the sample in a dry ice – acetone cooled collector and (b) absorbing this sample in a scrubber containing 0.01 N sodium hydroxide. An aliquot of this solution was backtitrated with 0.01 N hydrochloric acid solution to the phenolphthalein end point. The results were calculated as formic acid.

Peroxide Analysis

Liquid air was again used for condensation and the sample was run into a scrubber containing isopropyl alcohol. An aliquot of this solution was analyzed by iodometric titration. Since the peroxide content of the effluent in the conditions of these experiments proved to be negligible, the more sensitive test of Widmaier and Mauss (10) was also applied. Again, results indicated the absence of peroxides.

PRODUCT IDENTIFICATION

The qualitative analysis of the oxidation products was effected using several techniques and is still not quite complete. The Bendix time-of-flight mass spectrometer, applied as described by Gohlke (11), successfully identified several compounds. At 100 intervals during the running of the chromatograms the column effluent was leaked into the mass spectrometer and a full mass spectrum of the compound was obtained by a very sensitive amplification and rapid-scan method. A representative spectrum which was identified as that due to 2-methyl tetrahydrofuran is shown in Fig. 4.

Our experience in the interpretation of spectra from the time-of-flight mass spectrometer leads to the following conclusions:

(a) Several compounds may be scanned at the same time if the chromatographic column does not have sufficient resolving power. However, by comparing scans taken at the beginning and end of a peak elution this can be detected more easily than by conventional mass spectrometer.
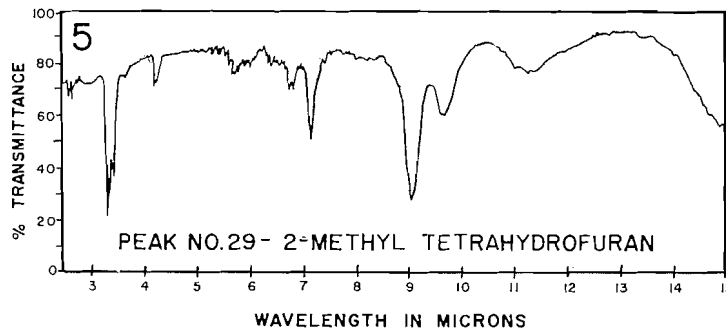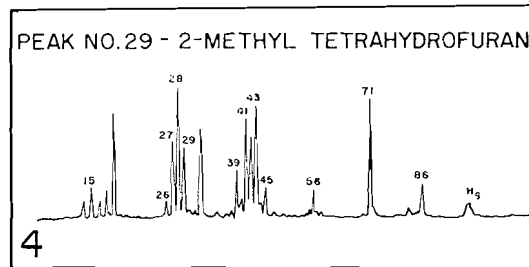
FIG. 4.   Representative time-of-flight mass spectrum.
FIG. 5.   Representative micro-gas-cell infrared spectrum.

(b) The accelerating chamber or the spectrometer lead-in is not completely swept between samples. As a result, there is a doubt as to whether any given peak is retained from a previous scan.

(c) With the mass scale used in our analyses, the numerical value of mass numbers greater than 80 was uncertain. We have, however, been informed that wider mass scales are now available.

(d) The background peaks gradually change in height when a number of scans is taken. There is therefore no way of knowing which contribution of a given mass is due to background and which to the component. This fault is also to be found, to a lesser extent, with conventional mass spectrometers.

Despite the above comments, the time-of-flight mass spectrometer has great potentialities for use in this field. The identity of most of the peaks analyzed by this means was confirmed by trapping the compound as it left the column and analyzing it by conventional mass spectrometer. For small peaks adjacent to large ones, however, the time-of-flight machine had a decided advantage.

In addition to the above analyses, the identity of seven of the peaks was confirmed by using a combination of gas chromatography and infrared spectrophotometry. Samples of the effluent from the chromatographic column were passed directly into a 600-mm path-length infrared micro-gas-cell designed by White (12). These were analyzed in a Beckman IR 4 infrared spectrophotometer equipped with a micro-optical system.

The spectrum of a representative reaction product peak, 2-methyl tetrahydrofuran, is shown in Fig. 5. It should be emphasized that the procedure described above was purposely adopted for convenience of sampling, i.e. to eliminate the troublesome sample freeze-out and transfer steps usually required. To do this, optimum spectrophotometric operating conditions were abandoned. Thus, for example, sample pressure was one atmosphere (mostly helium) rather than 50–100 mm Hg as usually recommended.

The infrared spectra thus obtained were correspondingly poorer than they might have been. Better resolution is obtained by trapping the samples in a liquid-air-cooled vessel, which may subsequently be evacuated while cool to remove helium and from which the sample may be flashed into the evacuated micro-gas-cell to the optimum pressure.

Further confirmation of the identity of any suspected component was obtained, whenever a sample of the pure compound was available, by comparison of their retention times relative to that of n-pentane. The compounds listed in Table II were identified by one or more of the above techniques. The relative retention times (n-pentane = 1) for these compounds are included in Table II. These values are the averages of from 5 to 15 determinations each, with deviations, generally, of less than $\pm 5\%$.

QUANTITATIVE EVALUATION OF RESULTS

To convert component peak areas to component concentrations, known volumes of pure compounds were analyzed under conditions similar to those used for the oxidation product mixture and calibration factors were then calculated. With eluent gas flowing through the column and the collector in a liquid-air bath, the standards were injected on to the heated connecting tube through a silicone seal in the liquid sampling cell and the eluent carried them into the collector where they were condensed. They were then transferred to the column by the technique already described. When the actual compound to be measured was not available in the pure state a similar type of compound was used as a standard. Where the peak was not positively identified the figures used for molecular weight and density in the calculation of selectivity were estimated on the basis of the suspected values. The concentrations were calculated by weight ratio. Generally areas were estimated as the product of peak height and peak width at half height. Where the base line undulated, the areas were measured by planimeter. For the water peak a piece of paper equal to the peak in area was weighed and for the earlier peaks, peak height was more convenient to measure than area.

RESULTS AND DISCUSSION

The state of the surface of the reactor is known to affect the initial rate at which oxidation occurs. The material of the reactor, together with the interrelated shape, mixture residence time, and flow configuration also affects the course of the reaction. When the reactor was first used it was found to give erratic results. Stability of the surface was rapidly obtained, however, when a little nitric acid was introduced at about 500° C and the temperature was slowly raised to 1000° C. After cooling the reactor to 500° C, a of stream helium was passed through until no chromatographic peak due to the nitric acid was obtained from a sample of the effluent.

On establishing that a fairly stable and reproducible surface could be prepared in this way, at least for the reaction of rich mixtures of pentane and air, a preliminary program was outlined for demonstrating the effectiveness of the gas chromatographic method and for obtaining new information regarding the effect of temperature on the product distribution from the reaction of one particular mixture of n-pentane and air. This program consisted of a series of runs at certain temperatures between 375 and 800° C with a 1.3 stoichiometric n-pentane – air mixture supplied to the reactor at the rate of 100 ml/ minute as measured at 25° C and 1 atmosphere pressure. Product analyses were carried out on samples of the effluent from each run as outlined previously using both gas chromatographic and chemical methods.

A representative chromatogram of the oxidation products of n-pentane obtained from

a run at a maximum reactor wall temperature of 509° C has been given in Fig. 3. By reference to Table II, which gives the key to the peak numbers, an idea of the mixture complexity and of the particular value of this method of analysis may readily be obtained. The results of calculations made from a series of such chromatograms in conjunction with those obtained from the chemical analyses are presented in Table III and Figs. 6–9.

TABLE III

Carbon balances
(carbon selectivity, %)

Temperature, °C	450	500	550	600	650	700	750	800
Oxides of carbon	22.5	15.4	12.0	9.8	8.7	16.0	55.2	71.6
Aldehydes and ketones	24.2	24.9	23.4	20.1	15.8	9.7	2.6	0.1
Methyl alcohol	8.4	5.4	2.2	0.4	—	—	—	—
2-Methyl tetrahydrofuran	17.8	20.0	18.6	14.2	9.0	3.5	—	—
Methane	—	—	—	—	1.2	4.0	4.9	4.5
Acids	4.6	4.4	2.6	0.3	—	—	—	—
Olefins	15.4	21.2	28.2	35.5	43.2	33.2	13.3	9.1
Deficiency	7.1	8.7	13.0	19.7	22.1	33.6	24.0	14.7
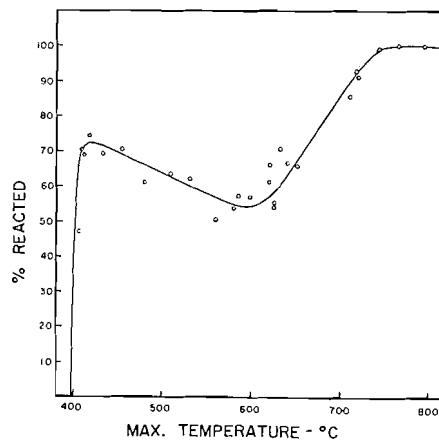
FIG. 6.   The effect of temperature on the percentage of *n*-pentane reacted.

In Fig. 6 the percentage of pentane reacted is plotted against maximum reactor wall temperature. The curve for *n*-pentane reacted rises sharply to a maximum at 410° C and then falls off slowly as the temperature increases to 625° C demonstrating again the now familiar negative temperature coefficient of the reaction in these conditions. From this point the percentage of pentane reacted rises sharply to 100%. The second sharp rise in the curve occurs when the mechanism of the over-all process changes so that carbon monoxide, carbon dioxide, and water become the major oxidation products.

The variations in product distribution with reactor temperature are indicated in Figs. 7–9. Several facets of the results deserve comment.

1. The absence of peroxides is significant in view of the proved sensitivity of the methods of detection employed. However, on the basis of former studies with a reactor of high surface-to-volume ratio (2), this result was not unexpected.

2. The surprisingly high concentration of 2-methyl tetrahydrofuran in the products, which accounts for as much as 20% of the carbon content of the *n*-pentane reacted, Table III, should be noted. The conditions of high surface-to-volume ratio and nitric acid pretreatment of the surface seem to favor the formation of this product.
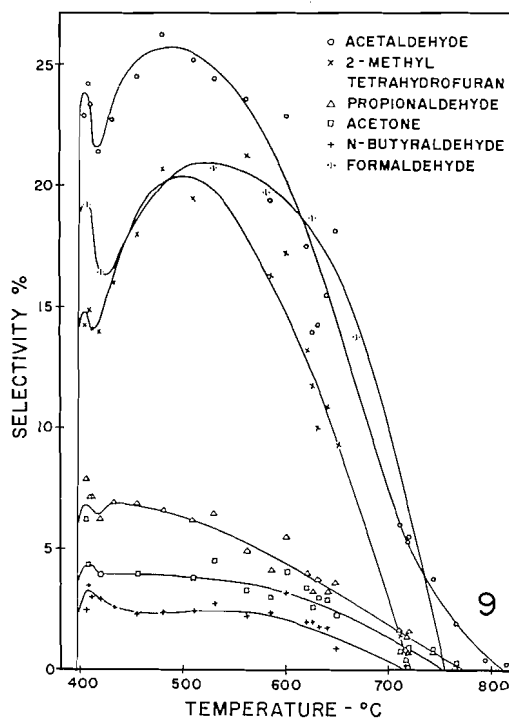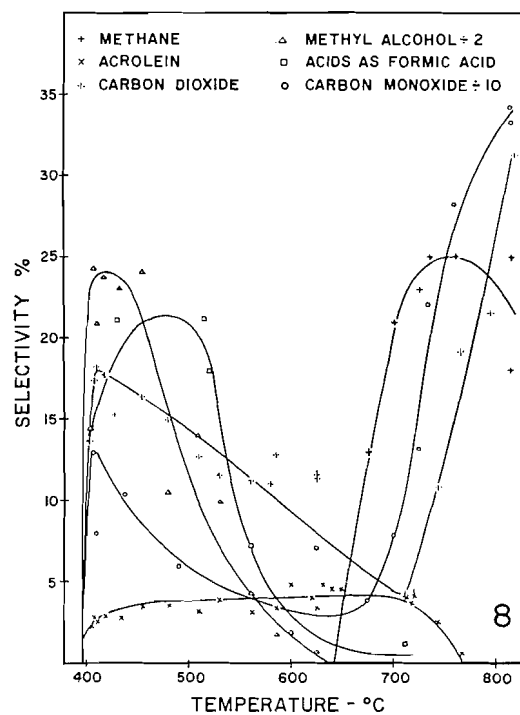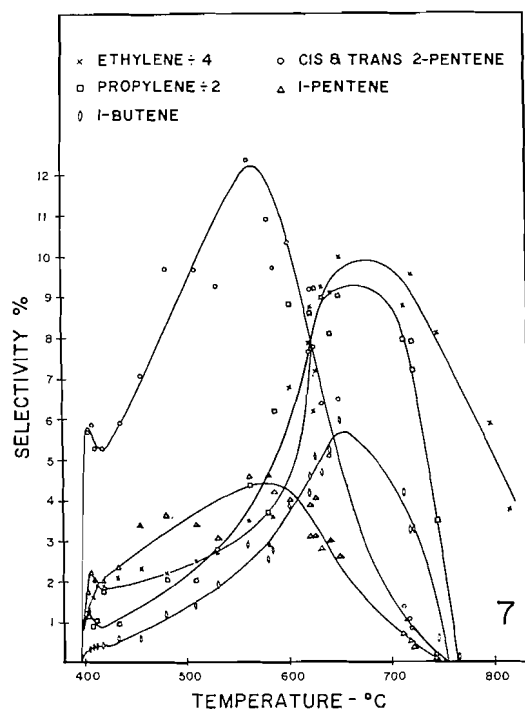
FIG. 7. The effect of reactor wall temperature on olefin selectivity.
FIG. 8. The effect of reactor wall temperature on product selectivity.
FIG. 9. The effect of reactor wall temperature on product selectivity.

3. A small but quite distinct dip in the product selectivities (Figs. 7 and 9) for the olefins and oxygenated compounds other than the acids, methanol, and oxides of carbon occurs at about 420° C. This is followed by a rapid increase in product concentration to a maximum and finally by a more gradual decrease.

4. A two-stage reaction mechanism, at least, is indicated. Methane is a product of the high-temperature reaction. Its formation is not evident below about 650° C (Fig. 8). On the other hand, the rate of formation of methanol and organic acids becomes negligible at this temperature. It is interesting that the high methane concentration in the high-temperature region is not accompanied by a correspondingly high hydrogen content (the hydrogen concentration was not detectable). This is further confirmation of the view that the lower olefins are formed via an oxidation mechanism and not by simple pyrolysis of the hydrocarbon in this temperature range.

5. The rate of formation of the simple olefins, ethylene, propylene, and butylene, becomes a maximum at about 700° C and the mechanism at higher temperatures appears to involve the further oxidation of these olefins. Ethylene is the most stable in this regard. The higher olefins attain their maximum concentrations at lower temperatures (550°–600°). When the concentration of the simpler olefins has reached a maximum that of the higher olefins has become negligible.

6. Epoxides, such as ethylene and propylene oxides, which were postulated by Boord (13) and observed by Kyryacos, Menapace, and Boord (7), were not found in the present study but may have escaped detection since they come off near the large acetaldehyde peak.

7. The relatively constant acrolein concentration (Fig. 8) over the wide range of temperature between 400 and 700° C is remarkable. An explanation for this observation is not available at this time.

8. The relative preponderance of carbon monoxide over carbon dioxide in the products (Fig. 8) is consistent with the results expected from the oxidation of a rich mixture.

9. Carbon balances on the identified products of the reaction for selected temperatures from the product selectivity – temperature graphs are given in Table III. A useful and rapid means of obtaining these carbon balances has been employed here. This is the concept of a carbon selectivity of a particular product, which may be defined as the product of component percentage selectivity and the ratio of the number of carbon atoms per mole of component and reactant respectively. Considering the omission from this tabulation of the carbon in the minor and the unidentified components and in those compounds less volatile than water, these balances indicate that this method of analysis can be used to provide the detailed information required to study the kinetics and mechanism of complex reactions.

CONCLUSION

1. The purpose of this preliminary work was to develop an integrated apparatus for the investigation of an oxidation or decomposition reaction with the principal aid of the gas chromatographic technique. In this respect a method of sampling has been described which will obviate many of the difficulties associated with the transfer of gaseous or liquid samples from the reactor to the gas chromatographic apparatus and will also allow samples to be taken for the more usual chemical or physical methods of analysis. Most of the condensable products may be analyzed in a single-stage process by a simple column-temperature programming technique.

2. The use of several qualitative microanalytical methods including time-of-flight

mass spectrometry and infrared spectrophotometry for identifying the products separated by the gas chromatographic method has been described and critically evaluated.

3. Although a mechanism for the reaction studied here will not be presented until further studies involving the effects on product distribution of varying the mixture strength, residence time, and condition of the surfaces have been completed, some of the interesting features of the results have been discussed. Thus, a method of obtaining a reproducible surface has been described, variations in product distribution with temperature have been noted, and the presence of certain suspected and some unsuspected compounds in the reaction product mixture has been confirmed or determined.

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