Products of Flash Pyrolysis of Phenol–Formaldehyde by Time-of-Flight Mass Spectroscopy*

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Synopsis

A sample of phenol–formaldehyde was flash-pyrolyzed 11 times in the reaction chamber of a time-of-flight mass spectrometer. Quantitative analyses were determined for pyrolysis products which were present within 10 sec. after each flash. A high degree of consistency between compositions of products from consecutive flashes resulted. The significance of the results is discussed.

Introduction

Thermal decomposition of plastics is generally accompanied by evolution of gaseous products. Knowledge of the chemical structure and quantity of these products is required for a number of practical applications and may give insight to the mechanism of decomposition. Although some decompositions are characterized by evolution of a single product, e.g., monomer, a large number of degradation products are produced in many cases. Some products may be unstable or reactive, thus storage may introduce errors in chemical analysis.

Since mass spectrometers have long been used to provide chemical analysis of complex decomposition mixtures, the high speed of operation of time-of-flight mass spectrometers suggested the use of this type of instrument for such studies. Examples of the success of time-of-flight mass spectroscopy with short-lived intermediates of several reactions may be found in the work of Kistiakowsky and co-workers.[1-3]

As the author was interested primarily in high temperature decomposition, radiation from xenon-filled flash lamps was used as the source of energy. Nelson and co-workers[4-6] have demonstrated the practicality of this form of heating.

Apparatus and Experimental Procedure

A somewhat modified Model 14–100 Bendix time-of-flight mass spectrometer was used for these studies. It was equipped with a Model 112 two-
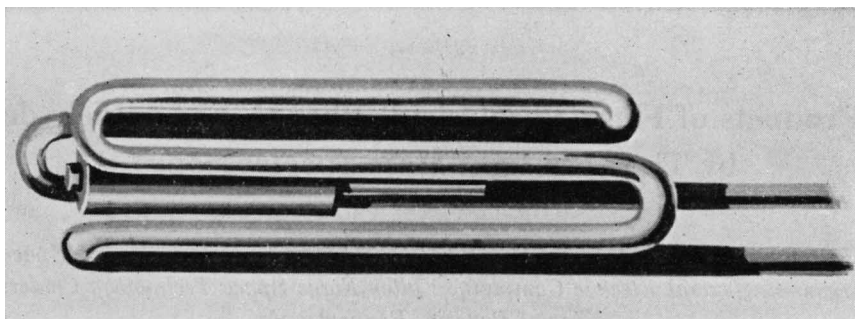

Fig. 1. Lamp coil geometry.

channel analog output system and a Model E-104 trap current regulator. The Model 321 scanner analog channel was used as is, while the Model 311 controller analog channel was converted to a second scanner. A Model 450 Hewlett-Packard amplifier was used to amplify the signal which was generated by the multiplier. The d.c. voltages throughout the instrument were kept constant by use of a Model CU1 Sola constant voltage transformer. Several small modifications were made to reduce noise and increase stability.

At the start of this study, it was hoped that it would be possible to analyze very unstable products, such as free radicals. Experience showed, however, that the sensitivity of this instrument was too low for that purpose;* however, the flash lamp was designed with that objective in mind. A drawing of the flash lamp coils with a sample in place is shown in Figure 1. A schematic diagram of the flash lamp and sample as mounted in the reaction chamber of the mass spectrometer, are shown in Figure 2. A complete description of the flash lamp will be published.[8] In operation, the assembly was placed in the reaction chamber of the mass spectrometer with a solid sample in place. The glass lead from the hollow electrode was fastened to the external vacuum system and the lamp evacuated at 10^{-6} mm. Hg for several hours. Meanwhile, the reaction chamber was evacuated through the mass spectrometer leak and through the reaction chamber pumping port by the external vacuum system. The lamp was then filled to about 40 mm. Hg with xenon. A 220 μF. capacitor bank at 5000 v. was discharged through the lamp in order to produce the flash.

A single 2-mil diameter gold foil leak was used for these experiments. The decomposition products were ionized with 70 v. electrons. All spectra were recorded with the ion lens of the mass spectrometer in operation. The liquid nitrogen trap of the mass spectrometer was filled as the lamp electrodes were being charged. The lamp was discharged 2 min. after the trap was completely filled, in each case. The analog spectra were recorded by the following method.

In normal operation, the multiplier received a new mass spectrum every

* Studier[7] recently described a continuous ion source which permitted the sensitivity of such mass spectrometers to be increased 300 times.
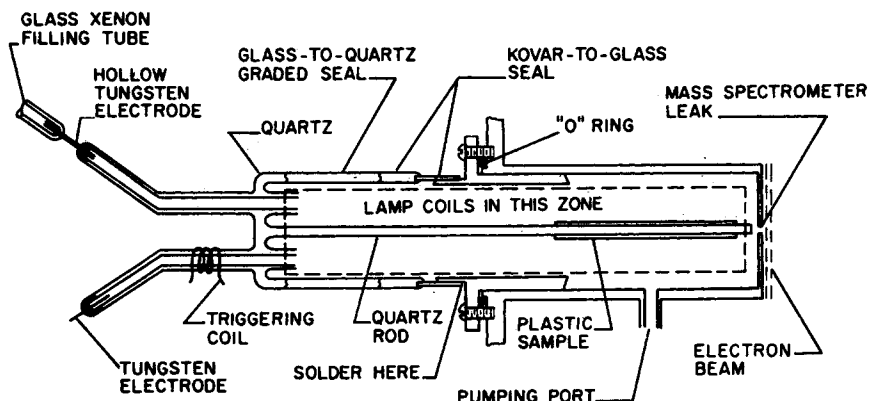
Fig. 2. Flash lamp and sample as mounted in reaction chamber of the mass spectrometer.

100 μsec. (10 Kcycles). The analog gate was activated only for a fraction of a microsecond during each mass spectrum and swept to either higher or lower mass numbers slowly from cycle to cycle. Thus, one may integrate a large number of events with the analog and increase the effective sensitivity. The starting mass may be selected manually by choice of an initial voltage. The mass range was swept by continually increasing or decreasing this voltage. The entire process was controlled by the 10 Kcycle master pulse of mass spectrometer. During flash pyrolysis experiments, it was necessary to start analog scan at the same time with respect to the flash for each flash experiment in order to obtain data that could be compared with a minimum of errors. The following procedure was found to give reproducible timing. The flash strikes a phototube, which generates a pulse. The pulse triggers the Tektronix Model 543 oscilloscope after a preset time delay (3 sec. for these experiments). A rising voltage which was generated by the oscilloscope, at a predetermined rate, replaced a similar voltage source in the analog and drove the gate towards an increasing mass range. A photograph of the mass spectrum was obtained by opening the camera shutter with the oscilloscope set for single sweep before striking the flash and closing the shutter after the desired mass range had been swept. It was desirable to use the second channel to study a greater mass range in shorter periods of time and to provide a wider range of sensitivity. Since the gate of the first channel was at the correct time relationship with respect to the master pulse, the gate signal of the first channel was used as a pulse to trigger the gate of the second channel. The starting mass of the second channel was set manually at the desired value. The gates of the two channels then began to sweep at the same predetermined time delay with respect to the flash and covered their respective mass ranges during the same interval of time. Calibration spectra were photographed in the same manner so that they could be compared with the unknowns more accurately. Analog channel 2, which covered the higher

mass range, was set to a higher sensitivity than channel 1. Channel 1 covered m/e 1–100, while channel 2 covered m/e 12–130. Analog sweep was completed in 7 sec. Reference samples of n-butane were run periodically to standardize the instrument.

A sample of pure phenol–formaldehyde was flash pyrolyzed 11 times in the reaction chamber of the mass spectrometer. Each flash was applied only after the products of the previous flash were pumped away, a process which took about $1/2$ hr. The mass spectroscopy data were analyzed by the following method.

Analysis of Spectra

Calibration samples of pure hydrogen, methane, carbon monoxide, ethane, ethylene, acetylene, water, and carbon dioxide were run in order to obtain their mass spectra. Comparison of these spectra with the mass spectral tables of the American Petroleum Institute showed that they were quite similar to spectra which were obtained at the National Bureau of Standards. Therefore, N.B.S. spectra were used for compounds which were not tested directly. Where N.B.S. spectra were not available, those spectra which were found to be most like N.B.S. spectra, for other compounds, were used. Note that the A.P.I. mass spectral tables were used only for minor components, so that small discrepancies in the pattern and sensitivity would not be too important. Direct calibration spectra were obtained by a technique which simulated part of the flash pyrolysis experiment. Samples of known pressure were introduced to the reaction chamber from the 3-liter reservoir. At the appropriate moment, the valve which separates the reaction chamber from the reservoir was closed. The analog system was triggered manually at that instant, and the oscilloscope was triggered after a time delay of 3 sec.

The first few analyses of data were performed by starting at the high mass end and assigning peaks to the compounds from which they probably originated. The lower mass fragment contributions which could be attributed to these compounds were then subtracted from the remaining mass spectrum in order to see if the choices were reasonable. Changes were made when necessary. When a consistent set of compounds was obtained for several flash experiments, a matrix was derived for application to the other flash experiments.

Results and Discussion

The results of these experiments are shown in Figures 3–5. Relative yields are given in Table I. Examination of the individual yields shows several trends. H_2, CO, CH_4, C_4H_2, C_5H_6, C_6H_6, C_7H_8, and C_8H_8 show a maximum yield at about the fourth flash with comparatively smooth increases in the earlier flashes and decreases in the later experiments. C_4H_4, C_4H_6, and C_5H_8 showed the same general behavior as the above, with several small variations. H_2O, CO_2, C_2H_2, and C_3H_8 showed a more or less continual decrease in yield. C_2H_4, C_2H_6, C_3H_4, and C_3H_6 showed an early

TABLE I

Degradation Products from Flash Pyrolysis of Pure Phenol–Formaldehyde Sample
as Determined by the Bendix Time-of-Flight Mass Spectrometer

Com-ponent	Products, mole-% in successive flash numbers										
	1	2	3	4	5	6	7	8	9	10	11
H₂	26.5	37.7	44.1	43.2	46.1	47.6	49.2	50.7	52.7	52.9	53.3
CH₄	6.0	7.9	9.3	10.3	10.1	9.3	9.1	9.3	10.3	10.1	9.5
H₂O	31.3	19.8	12.5	12.1	11.0	9.9	7.4	8.8	9.0	7.4	9.5
CO	16.7	23.1	23.1	24.4	22.6	22.8	22.2	18.1	16.9	17.0	17.9
C₂H₂	4.0	2.3	2.0	1.5	1.5	1.8	2.2	1.8	1.4	1.7	1.0
C₂H₄	3.9	1.7	2.1	1.8	1.9	1.1	1.5	3.1	2.2	2.9	2.0
C₂H₆	2.1	1.2	1.3	1.2	1.3	1.6	1.8	1.9	1.9	2.0	1.4
C₃H₄	0.7	0.2	0.4	0.4	0.3	0.5	0.5	0.6	0.5	0.5	0.4
C₃H₆	1.7	0.9	0.6	0.6	1.0	1.0	1.4	1.5	1.2	1.5	0.8
C₃H₈	1.7	0.8	0.7	0.7	0.7	0.8	0.9	0.8	0.6	0.7	0.5
CO₂	4.2	2.4	1.7	1.4	1.3	1.3	1.3	1.2	1.2	1.3	1.5
C₄H₂	0.1	0.1	0.2	0.2	0.2	0.2	0.2	0.2	0.1	0.1	0.1
C₄H₄	0.1	0.2	0.2	0.2	0.1	0.2	0.2	0.1	0.1	0.2	0.1
C₄H₆	0.1	0.2	0.1	0.2	0.2	0.2	0.2	0.2	0.2	0.1	0.2
C₄H₈	0.3	0.3	0.5	0.4	0.4	0.4	0.6	0.5	0.4	0.5	0.3
C₅H₆	0.1	0.3	0.3	0.3	0.3	0.4	0.4	0.4	0.4	0.4	0.4
C₅H₈	0.1	0.3	0.5	0.6	0.5	0.2	0.3	0.2	0.3	0.2	0.4
C₆H₆	0.2	0.4	0.2	0.2	0.2	0.5	0.4	0.4	0.4	0.4	0.4
C₇H₈	0.1	0.1	0.1	0.2	0.2	0.1	0.1	0.1	0.1	0.1	0.1
C₈H₈	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Avg. pressure, mm. Hg,ᵃ	3.54	4.15	4.14	4.48	3.84	3.43	2.81	2.35	2.05	2.01	2.14

ᵃ Average pressure in reaction chamber during analog sweep; pressure relative to room temperature.
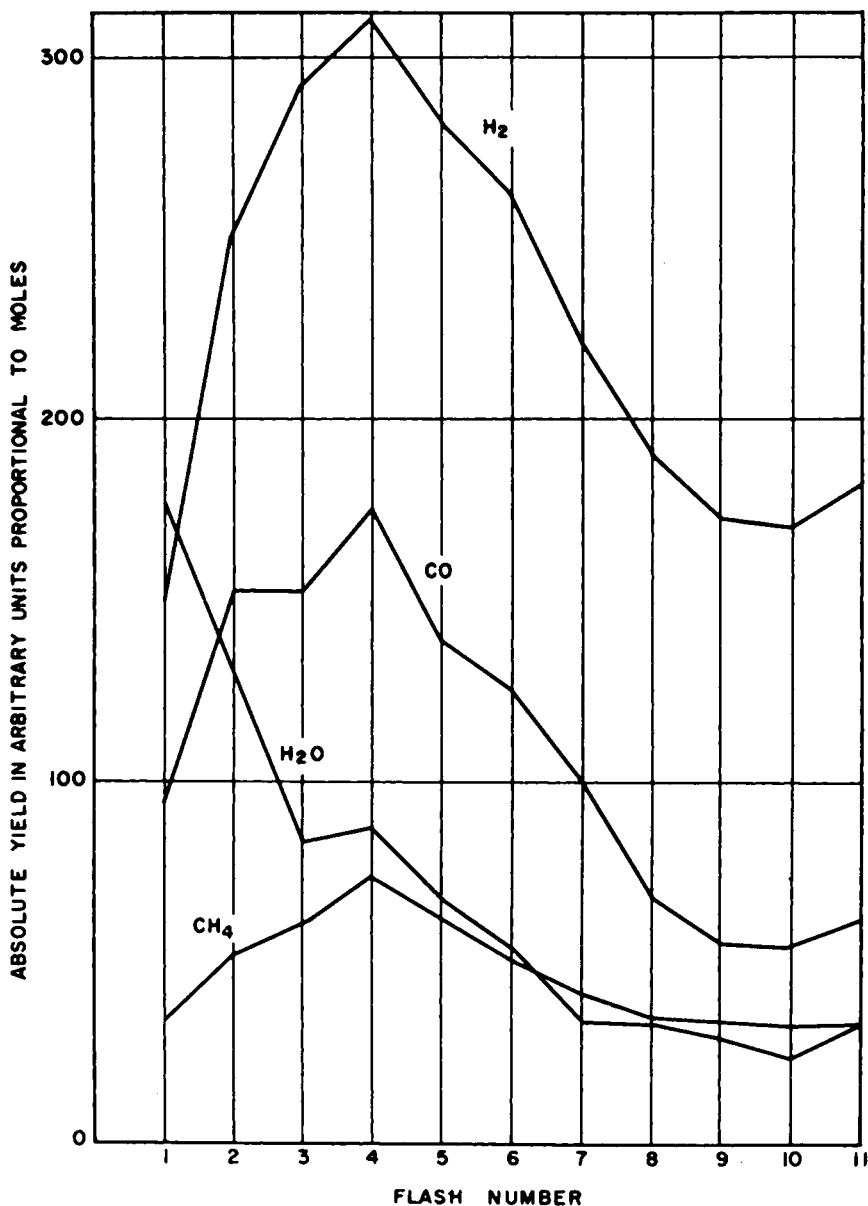
Fig. 3. Product yields from flash pyrolysis of phenol–formaldehyde (H_2, H_2O, CO, CH_4).

decrease in yield, followed by a leveling off and then a comparatively grad-
ual decrease. C_4H_8 showed a rather different trend.   The yield of C_4H_8
was very irregular with the maximum yield at the seventh flash.   In gen-
eral, however, H_2, CO, CH_4, and C_4 and heavier hydrocarbons showed one
type of behavior, while H_2O, CO_2, C_2, and C_3 hydrocarbons showed a
different type.   This information could conceivably lead to understanding
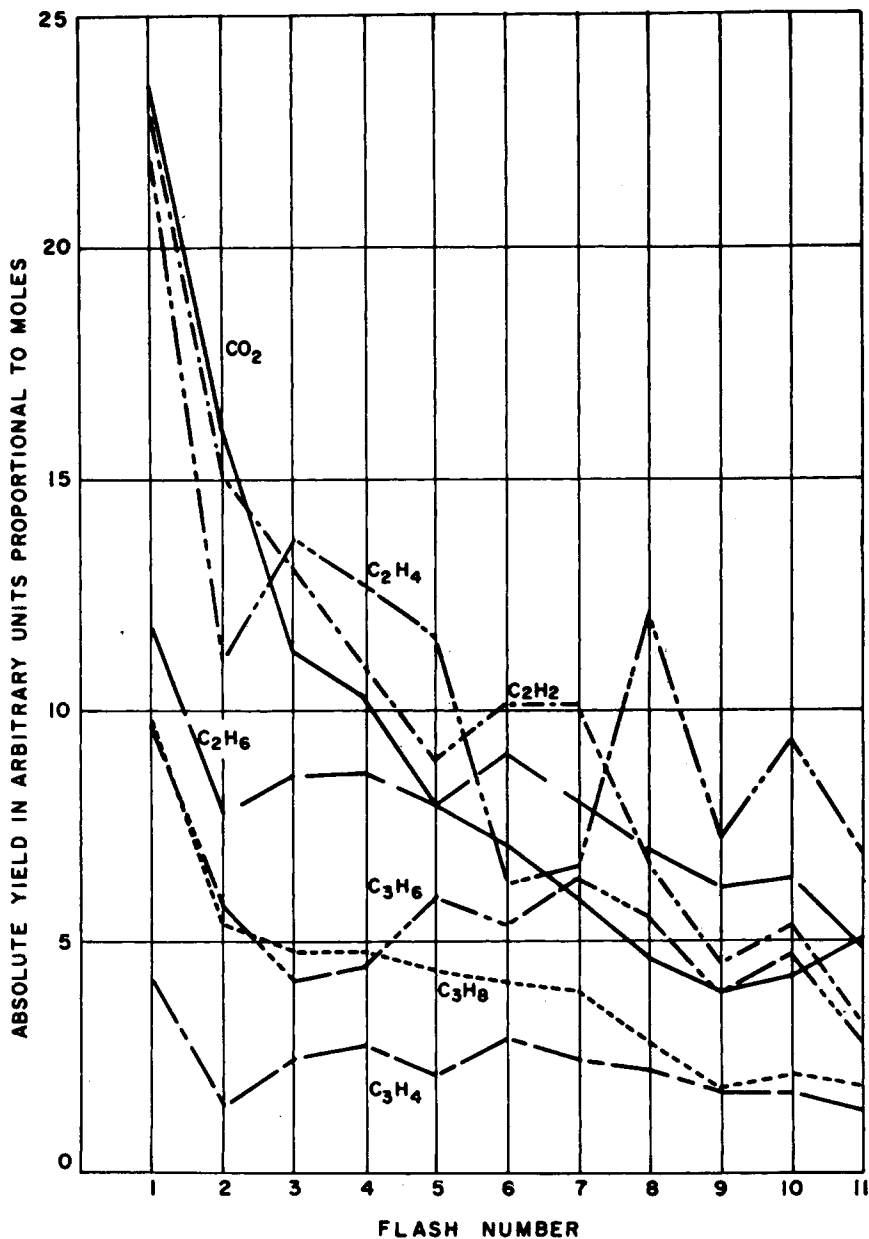
Fig. 4. Product yields from flash pyrolysis of phenol–formaldehyde (CO_2 and C_2 and C_3 hydrocarbons).

of the mechanism of high temperature degradation of phenol–formaldehyde and other complex plastics. The early appearance of H_2O and CO_2 was consistent with observations of Ouchi and Honda.[9] These authors also found that H_2, CO, and CH_4 formed later, and at about the same time.
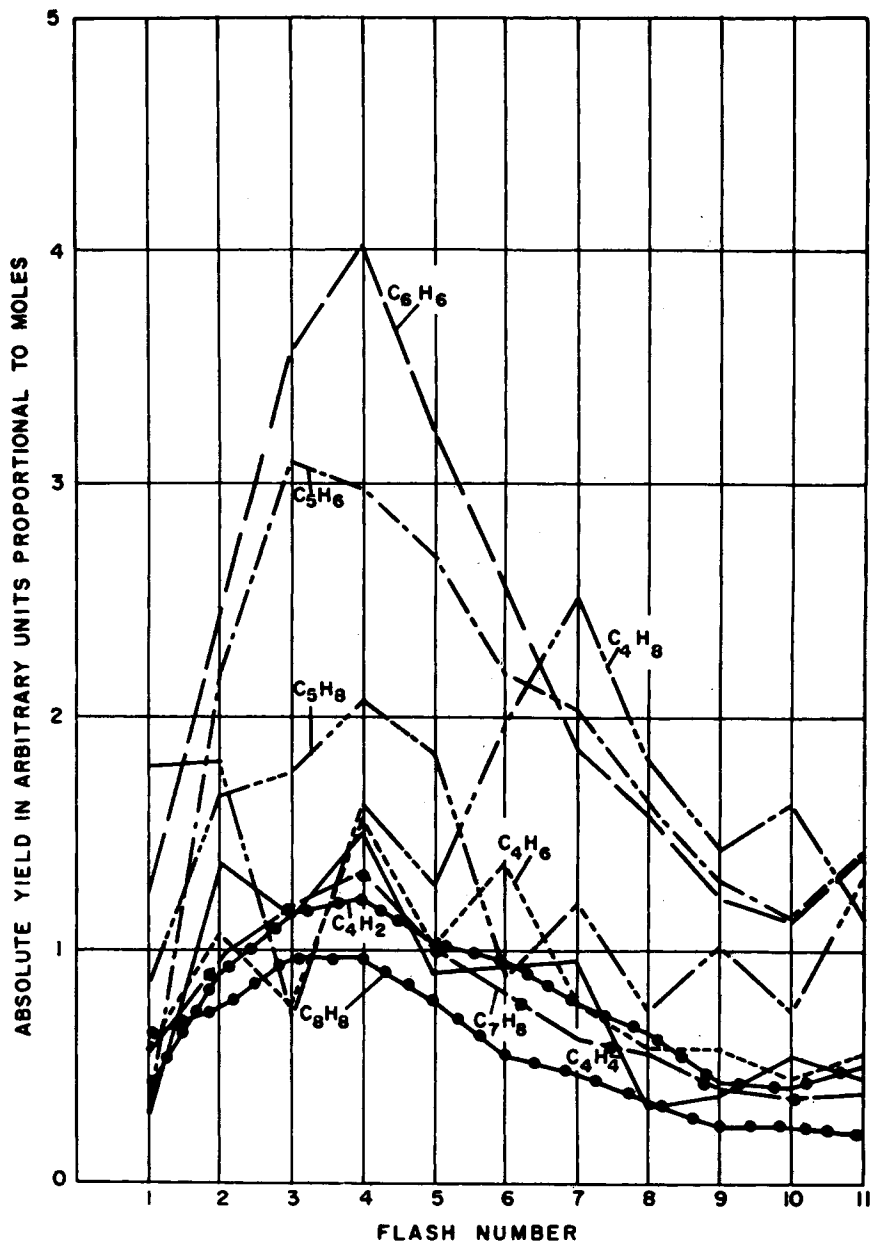
Fig. 5. Product yields from flash pyrolysis of phenol–formaldehyde (C_4–C_8 hydrocarbons).

Although the analytical data show great consistency, there are several possible sources of error. One type of error is normal instrumental error. Another source of error may be chemical reactions which occur among the products during the time of analog scan.   A further source of error may be

TABLE II

Comparison of Arc-Image and Flash Pyrolysis

Component	Relative yield, moles/mole H_2 with arc-image furnace	Relative yield, moles/mole H_2 in successive flash numbers										
		1	2	3	4	5	6	7	8	9	10	11
H_2	1	1	1	1	1	1	1	1	1	1	1	1
CO	0.377	0.629	0.612	0.523	0.566	0.490	0.478	0.451	0.356	0.321	0.320	0.336
CH_4	0.244	0.266	0.210	0.210	0.238	0.218	0.195	0.185	0.183	0.195	0.191	0.179
Fraction 2[a]	0.198	0.714	0.272	0.212	0.196	0.188	0.192	0.219	0.234	0.186	0.217	0.158
Fraction 3[b]	38.6[c]	23.3[c]	11.9[c]	7.9[c]	7.9[c]	6.9[c]	5.9[c]	4.9[c]	5.1[c]	4.9[c]	4.1[c]	5.1[c]

[a] Fraction 2 in arc-image furnace experiment consists of components which are not volatile at liquid nitrogen temperatures and distill from a CO_2 ice-cooled trap. For the flash pyrolysis experiments, this fraction is assumed to contain all C_2, C_3, and C_4 hydrocarbons and CO_2.

[b] Fraction 3 in arc-image furnace experiment consists of components which are not volatile at CO_2 ice temperatures and distill from a trap at room temperature. For flash pyrolysis experiments, this fraction is assumed to contain all C_5 and heavier hydrocarbons and H_2O.

[c] Yield in g./mole H_2.

caused by continued generation of gases from the hot surface long after the flash is extinguished. Another type of error is due to the fact that the lighter gases will be pumped out of the 100 cc. reaction chamber through the 2-mil diameter leak more rapidly than the heavier gases. Flow tests showed that this error is not very large and is rendered less serious than otherwise because the lighter masses are scanned earliest.

A sample of the phenol–formaldehyde was pyrolyzed in the Space Sciences Laboratory arc-image furnace facility according to the procedure which has been described elsewhere.[10] A partial qualitative analysis disclosed the presence of H_2, CO, CH_4, N_2 (traces), CO_2, C_2H_2, C_2H_4, C_2H_6, H_2O, benzene, styrene, toluene, and xylene. Quantitative comparisons of some of the products with those of the flash pyrolysis experiments are listed in Table II. The agreement of results is very good, considering the differences in the experiments. Because of the pumping error associated with the analog readings, the relative yields of the flash experiments are probably slightly too low.

Different samples were found to give somewhat different product distributions and yields in flash pyrolysis. Examinations of different samples after pyrolysis suggested that the finish of the surface influenced the absorption of energy. In some cases, the surface appeared to be blackened rather uniformly, while in others, some parts were hardly blackened. Machining notches, which were readily discerned by the eye, appeared to be readily blackened. It would certainly be helpful to have a technique to produce a standard and uniform surface finish on samples if one desired to compare different samples of the same material. In addition, the energy flux is not uniform over the surface of the sample because of lamp geometry. Still, it would be helpful to know an average energy input and/or surface temperature.

Since H_2, H_2O, CO, and CO_2 were major decomposition products for the 11 flash experiments, temperatures were calculated based on the possibility that the water gas equilibrium was important. The water gas equilibrium

TABLE III
Surface Temperature Calculated from Water–Gas Equilibrium

Flash number	Temperature, °K.
1	2025
2	2090
3	1790
4	2030
5	1880
6	1755
7	1495
8	1480
9	1450
10	1305
11	1385

temperature would be valid if these four products came to equilibrium on the surface and then were cooled rapidly upon leaving the surface.   Equilibrium constants were calculated from the yields, and temperatures were determined from the literature.[11]   They are listed in Table III.   The temperatures and trend are thought to be quite reasonable.   One might expect that, during earlier flashes, the sample would start to blacken and might become a better receptor of radiant energy.   However, with each flash, solids which are driven off from the plastic surface could coat the lamp and may thus reduce its energy output.   A portion of the decomposition gases could come from the lamp surface and other surfaces of the reaction chamber.

Conclusions

As a result of these experiments, it is concluded that one may use a time-of-flight mass spectrometer to give reasonably accurate chemical analysis of a complex mixture of stable gases which are present within a short time after high temperature pyrolysis.   The main advantages of the method are its speed and the fact that the products need not be handled once they are generated.

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Résumé

Un échantillon de phénol-formaldéhyde a subi onze fois la pyrolyse-éclair dans la chambre de réaction d'un spectromètre de masse du type "temps de passage." On a opéré des analyses quantitatives des produits de pyrolyse qui étaient présents dix secondes après chaque pyrolyse. Un degré élevé de reproductibilité quant aux produits formés apparaît d'une pyrolyse à l'autre. On discute de la signification de ces résultats.

Zusammenfassung

Eine Phenolformaldehydprobe wurde elfmal in der Reaktionskammer eines Flugzeitmassenspektrometers flash-pyrolysiert. Quantitative Analysen wurden für Pyrolyseprodukte, die innerhalb von zehn Sekunden nach jedem Flash vorhanden waren, durchgeführt. Es ergab sich ein hoher Grad von Konsistenz zwischen der Zusammensetzung von Produkten aufeinanderfolgender Flashs. Die Bedeutung der Ergebnisse wird diskutiert.