Characterization of trimethylol phenol by thermal analysis

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Abstract

A study was made of the condensation and thermal behaviour of trimethylol phenol (TMP) as a model of a phenol–formaldehyde (PF) resin. Results of study by the combined techniques of differential thermal analysis and thermogravimetry, without resorting to spectroscopic or chromatographic methods, clearly corroborate existing theories regarding the mechanism of curing of PF resins, but in addition it proved possible to attempt a quantitative evaluation of the thermoanalytical behaviour of TMP in air. The relative reactivities of 2,2′-, 2,4′- and 4,4′-dimethylene ethers in their decomposition to methylene bridges are shown to decrease in the order 4,4′-> 2,4′-> 2,2′-. It is concluded that the purity and/or identity of any methylol phenol can be established by conventional combined DTA–TG measurements.

INTRODUCTION

Phenol–formaldehyde (PF) resin is a well known and important thermosetting resin. Both novolacs and resols are available in various grades which vary in both phenol to formaldehyde ratio and average molecular weight. Physical and chemical properties of the resins also vary accordingly. The curing of PF resins has been extensively studied and the mechanisms of self-condensation are fairly clearly understood. In the case of highly methylolated phenols, the increase in molecular weight occurs through intermolecular condensation–dehydration of two methylol groups. The reaction starts around 130°C, leading to the formation of methylene ethers [1]. The stabilities of methylene ethers have been reported to be limited up to a temperature of 160°C, beyond which they decompose to diphenylmethylenes with the liberation of one molecule of formaldehyde [2].

Hultzsch [3] has indicated that, in the presence of an acid or alkaline catalyst, quinone methides are also formed. Euler et al. [4] have suggested that formation of dimethylene ether, diphenyl methylenes and quinone

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methides can take place simultaneously. Elimination of water does not necessarily mean the formation of only the ether; formation of quinone methide is also possible, and this can subsequently react with another alcohol to give a methylene linkage with the elimination of formaldehyde. In any case, elimination of water and formaldehyde remain as the major events in the curing of methylol phenols.

Although these two major events have been established beyond doubt, the quantitative correlation of these processes and the temperature ranges of their occurrence could not be unambiguously ascertained. The major retarding factor is the polydispersity of the resin molecules in respect of degree of methylolation and molecular weights. An unambiguous and quantitative estimate of the intermolecular condensation of methylols and intramolecular elimination of formaldehyde, and the corresponding ranges of temperature for the onset and completion, can, however, be obtained from the thermal analytical behaviour of some model molecules of established chemical structures and molecular weights. In this regard, pure mono-, di- or trimethylolated phenols would be the obvious choice. In this communication, we report the condensation and thermal degradation behaviour of the fully methylolated phenol, i.e. trimethylol phenol (TMP), as a model phenol–formaldehyde resin. Mono- or dimethylolated phenols have not been considered for investigation because the methylolation at the three reactive sites in phenol, i.e. 2-, 4-, and 6-positions, takes place simultaneously, giving rise to a mixture of mono-, di- and trimethylolated products.

The technique used in this study is the conventional one of combined differential thermal analysis (DTA) and thermogravimetry (TG) without the aid of spectroscopic or combined chromatographic techniques. The results obtained clearly corroborate the existing theory of the mechanism of curing of PF resins, but on an almost quantitative scale.

EXPERIMENTAL

TMP was prepared following patented methods [5,6] with some modifications as reported by Conley and Bieron [7].

The TMP so produced was a transparent, highly sticky, highly viscous, light yellow–brown mass, insoluble in water but freely soluble in methanol, aqueous sodium hydroxide and ammonia. It is also soluble in dimethyl sulphoxide, dimethylformamide, acetone and acetic acid.

The identity of the product as a methylolated phenol was established by means of IR and NMR spectra (Table 1). The purity of trimethylol phenol could not be established by the NMR peak integration method. However, by thermogravimetric analysis (as will be shown later) the purity has been calculated to be almost 100%.

TABLE 1

IR and NMR spectral assignments of trimethylol phenol

Spectrum	Peak/band	Assignments	Literature values	Reference
IR [a]	3380 cm^{-1}	$-CH_2O-H$ stretch	3400 cm^{-1}	8
	3020 cm^{-1}	$-CH-$ (arom) stretch	3030 cm^{-1}	
	2930 cm^{-1} }	$-CH_2-$ stretch	2962 cm^{-1} }	
	2880 cm^{-1} }		2853 cm^{-1} }	
	1060 cm^{-1}	$-CH_2-O-H$ bending	1058 cm^{-1}	
NMR [b]	4.95 ppm	$2-CH_2OH$	5.1 ppm	9, 10
		$4-CH_2OH$	4.8 ppm	
	7.5 ppm	aromatic H	7.0 ppm	

[a] Bands at 1658, 1700 and 1710 cm^{-1} corresponding to benzophenone, quinone and carboxyl types of carbonyl stretching absorptions [14] are absent.
[b] DMSO-d_6 solvent.

Simultaneous DTA and TG traces of trimethylol phenol were recorded on Shimadzu DT-40 and DT-30 Thermal Analyzers in air and in argon atmospheres at a heating rate of 15°C min^{-1} up to 1000°C.

RESULTS AND DISCUSSION

The DTA and TG curves of TMP obtained in air at a heating rate of 15°C min^{-1} are presented in Fig. 1. The important thermal effects and corresponding temperature ranges together with the associated changes in mass are presented in Table 2.

Curing of trimethylol phenol

The data in Table 2 are self explanatory. In the range 30-108°C, no weight loss is observed and no physical or chemical transformation is apparent. At 108°C, an endothermic change ensues with the loss of weight, consistent with the observation of Millane [11]. The change is very sharp, and is complete at about 165°C. The corresponding weight loss is about 14.65%, compared with a theoretical water loss of 14.67% due to inter-molecular condensation of methylol groups. The observed temperature range is consistent with the reported one [2]. This endotherm is followed by three distinct exothermic transformations between 165 and 445°C with a total weight loss of 24.48%, which is almost equal to the 24.46% calculated for the loss of formaldehyde from the decomposition of dimethylene ether to methylene groups. Two points are noteworthy. First, all the changes in this temperature range are exothermic. Second, the whole process is split into three distinct steps. These features are typically absent in the thermo-
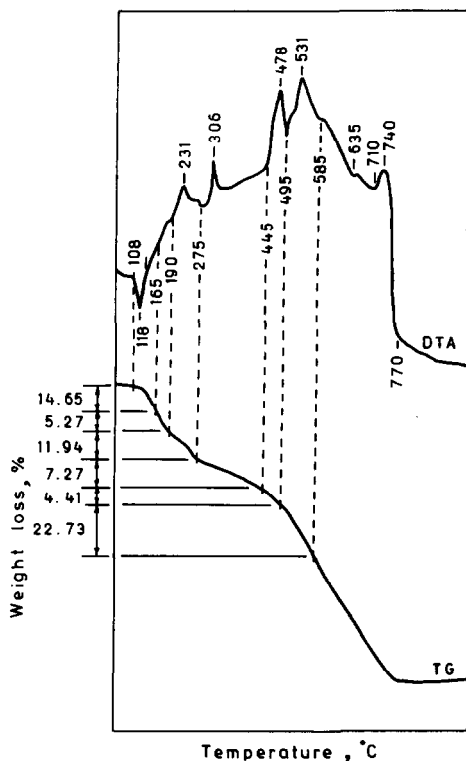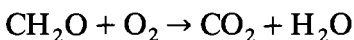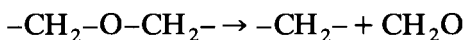
Fig. 1. DTA and TG curves of TMP obtained on heating in air at a rate of 15°C min^{-1}. Weight losses at various temperatures are indicated.

grams of TMP in an inert atmosphere (Fig. 2). The exothermicity of these stages may be attributed to the overall thermicity of the reactions

$$-CH_2-O-CH_2- \rightarrow -CH_2- + CH_2O$$

$$CH_2O + O_2 \rightarrow CO_2 + H_2O$$

The first reaction is weakly endothermic, while the second one is sufficiently exothermic for the overall reaction to be exothermic. In an inert atmosphere, the second reaction does not take place, and therefore the steps are virtually obscured. Further, the reactions are incomplete even up to 450°C in an inert atmosphere. An enhanced rate of splitting of CH_2O in air is possibly due to the formation of some –COOH groups [12] which, in sufficient concentration, can catalyze the splitting of CH_2O.

The second observation is important in that the relative reactivities of 2,2'-, 2,4'- and 4,4'-dimethylene ether bridges towards the formation of methylene linkages are easily discernible. On a statistical average, in a matrix of phenol moieties linked by dimethylene ether bridges, the relative abundances of the 2,2'- 2,4'- and 4,4'-bridges would be in the ratio 4:4:1. It is possible that, in the absence of any difference in specificity for these

combinations in the condensation–dehydration process, the above theoretically calculated relative ratio of 4:4:1 is likely to deviate to some extent because of growing steric limitations as condensation progresses. The experimentally observed ratio in the present study is, however, 4.39:2.67:1.94, which differs considerably from the theoretical value. Nevertheless, the general trend in the values indicates reactivities of various dimethylene ether linkages in the order 4,4'->2,4'->2,2'-, corresponding to temperature ranges of 165–190, 190–275 and 275–445°C respectively. The deviation from the theoretical ratios is attributed to local strains or steric effects associated with various dimethylene ether bridges in the cross-linked resin network, which is imposed over their normal reactivities.

The present observation of the temperature range for decomposition of dimethylene ether bridges is in excellent agreement with the reported one [2,12–15] of 160–440°C.

The combined weight loss due to condensation–dehydration and splitting of formaldehyde therefore accounts for 39.13% both in experiment and theory. This clearly establishes the purity of the TMP prepared and used in the present investigation.

Oxidative degradation of cured resin

Postcure degradation of phenol–formaldehyde resin has been intensively studied by Conley and co-workers [7,13,14] with the help of IR spectroscopy coupled with evolved gas analysis. The degradation effected was purely pyrolytic rather than oxidative since the evolved gases were obtained by continuous flushing of the reaction chamber by an inert gas such as helium. Degradation effected in the present study was, in fact, an oxidative one, and the general sequence and mechanism of degradation are liable to differ from those proposed by Jackson and Conley [14].

It is seen that the TG curve of TMP represents a continuous decrease in mass with no horizontal plateau, although the DTA curve (in air) presents distinct stages of degradation processes (Table 2). The stages almost overlap, and are unlikely to offer any quantitative correlations from the corresponding loss in weight in the TG curve. Nevertheless, an attempt may be made to gather some information about the changes that may take place in these stages of decomposition from the corresponding weight loss.

The exotherm in the range 445–495°C accounts for a weight loss of 4.41% or a weighted mass of 8.11 per mol of TMP (MW = 184). Such a low mass number can, however, be easily rationalized if the degradation of diphenyl methylene bridges is taken into consideration. Nakamura and Atlas [12] assigned this change to condensation of aromatic rings as the beginning of char formation after loss of methylene bridges. Elimination of any of the 2,2'-, 2,4'- and 4,4'-methylenes, along with ketonization of phenolic –OH groups, may give rise to binuclear quinones, as shown in Fig.

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TABLE 2

Thermal analytical characteristics of trimethylol phenol

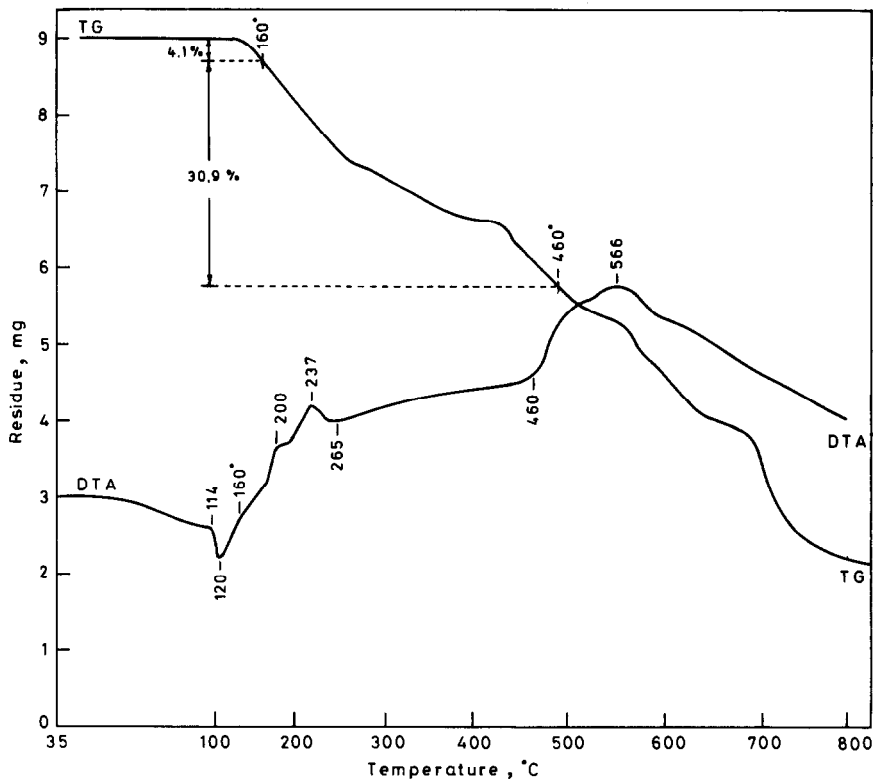| Serial No.	DTA		Probable reactions	TG, Wt loss (%)	
	Temp. range (%)	thermicity		Found	Theory
01	30–108	Nil	—	0	0
02	108–165	Endo	$-CH_2OH + HOCH_2- \rightarrow -CH_2-O-CH_2-O-CH_2 + H_2O$	14.65	14.67
03	165–190	Exo	$-CH_2-O-CH_2- \rightarrow -CH_2- + CH_2O$ $CH_2O + O_2 \rightarrow CO_2 + H_2O$	5.27	
04	190–275	Exo		11.94	24.46
05	275–445	Exo		7.27	(total)
06	445–495	Exo		4.41	4.40
07	495–585	Exo		22.73	22.82
08	585–665	Endo	Skeletal degradation	14.09	
09	665–715	Endo		10.48	
10	715–765	Exo		9.31	

Fig. 2. Thermograms (DTA and TG curves) of TMP in an inert atmosphere.

3. The corresponding loss of one CH_4 molecule would account for a mass of 8 from every TMP moiety. The observed mass loss of 8.11 is in excellent agreement with this theoretical value.

The fragment weight corresponding to the weight loss of 22.73% in the temperature range 495–585°C is similarly calculated to be 41.82 per mole of TMP. Degradation of the rest of the methylene groups, together with splitting of a C=O unit from the benzene ring, accounts for a mass of $14 + 28 = 42$, which is very close to the experimental value of 41.82.

It is difficult to ascertain from the thermograms whether the loss of methylene groups in the temperature ranges of 445–494 and 495–585°C does involve hydroperoxidation and subsequent ketonization as distinct stages. In all probability, the formation and degradation of hydroperoxides and benzophenone type ketones would be too fast at elevated temperature (445–585°C) and in the presence of atmospheric oxygen to be identified as separate stages in the thermograms. Formation of the binuclear quinone as represented in Fig. 3 is, however, consistent with many known organic reactions involving free radical mechanisms.

Evidence in favour of the decomposition mechanism is already available in the literature. First, CH_2O has been found to evolve in the pyrolysis of

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I.

HOH₂C—〔OH ring〕—CH₂OH + HOH₂C—〔OH ring〕—CH₂OH →(−H₂O)→ −O−H₂C—〔OH ring〕—C H₂ H₂ C—O—〔OH ring〕—CH₂O−

(CH₂OH below first and second rings; CH₂O− below product rings)

(2,2′−,2,4′−,4,4′− Condensation)

II.

〔OH ring〕CH₂.O.CH₂〔OH ring〕 —165−190°C / −CH₂O→ 〔OH ring〕CH₂〔OH ring〕

(2,2′− or 2,4′−)   (2,2′− or 2,4′−)

〔OH ring〕CH₂.O.CH₂〔ring OH〕 —190−275°C / −CH₂O→ 〔OH ring〕CH₂〔ring OH〕

(2,4′− or 2,2′−)   (2,4′− or 2,2′−)

HO〔ring〕CH₂.O.CH₂〔ring〕OH —275−445°C / −CH₂O→ HO〔ring〕CH₂〔ring〕OH

(4,4′−)   (4,4′−)

CH₂O + O₂ ———→ CO₂ + H₂O

III.

〔OH ring〕CH₂〔OH ring〕 —445−495°C / −CH₄→ 〔O ring〕=〔O ring〕

(2,2′− or 2,4′−) or 4,4′−   (2,2′− or 2,4′− or 4,4′−) binuclear quinone

CH₄ + 2O₂ ———→ CO₂ + 2H₂O

IV.

CH₂〔O ring〕=〔O ring〕CH₂ —495−585°C / −CO, −CH₂→ Condensed aromatic skeleton

CH₂   CH₂

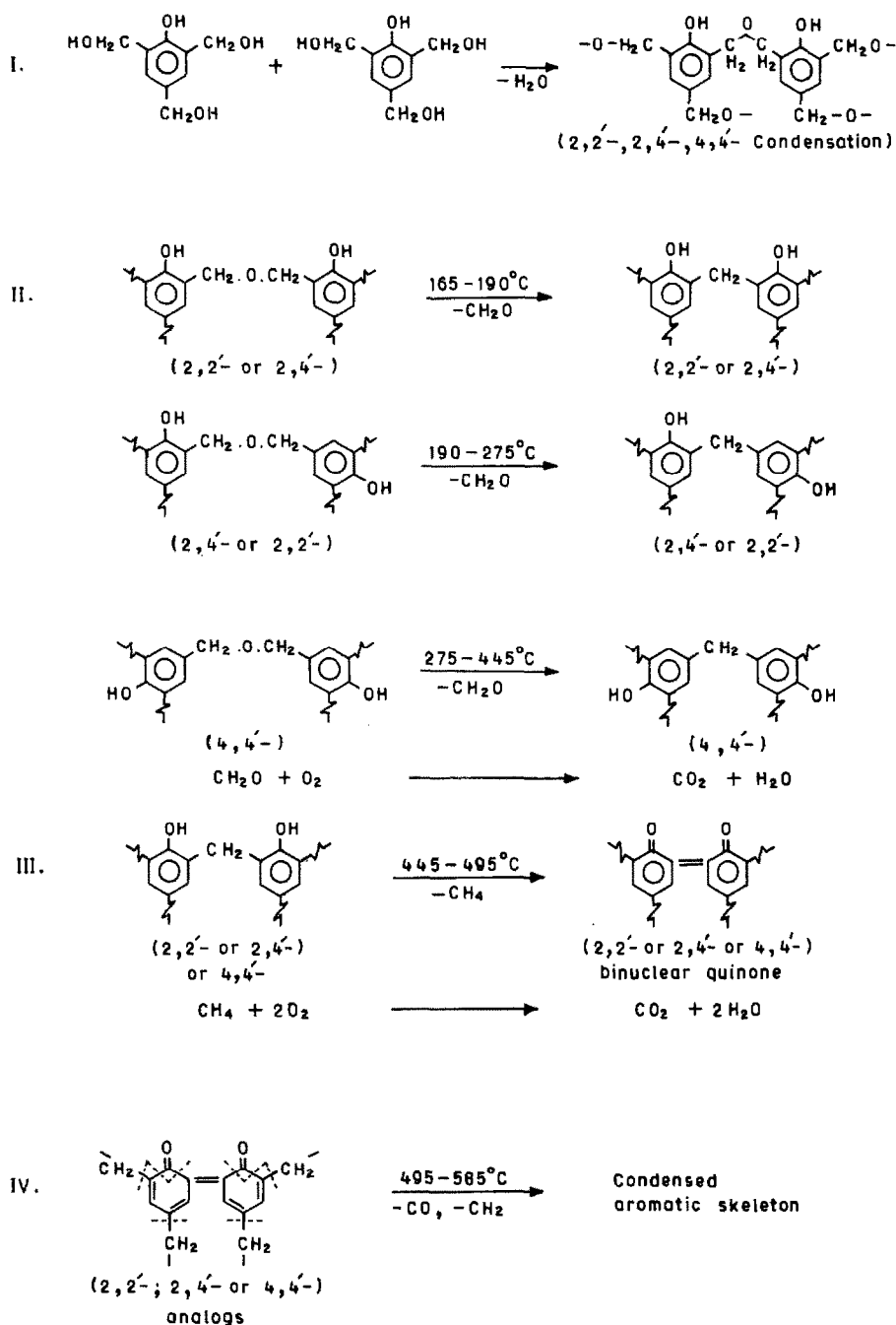(2,2′−; 2,4′− or 4,4′−) analogs

Fig. 3. Scheme showing the elimination reactions of TMP.

cured resin [15] up to a temperature just beyond 400°C, which may be compared with the range 165–445°C observed by us. Second, the splitting of CH₄ corresponding to step III (Fig. 3) in the range 445–495°C has been

substantiated by evolution [15] of CH_4 in the temperature range 375–475°C. Jackson and Conley [14] also reported that the anerobic degradation of cured PF resin yielded CH_4 starting from 400°C. Third, the detection of carbon monoxide [14] in the evolved gas above about 550°C is also consistent with the splitting of CO from the binuclear quinones beyond 495°C, as proposed by us. Slight differences in the temperature ranges are obviously due to the differences in degradation environment (air or inert gas) and in the heating rate.

The subsequent stages of decomposition in the temperature ranges 585–665, 665–715 and 715–765°C would be difficult to correlate with the corresponding thermogravimetric data owing to a very complicated and irregular skeleton of the degraded residue. The degradation of cured TMP, or PF resins in general, may therefore be represented schematically as in Fig. 3.

The sequence of curing and the stages of degradation as proposed here are based purely on an attempted quantitative evaluation of the thermal analytical behaviour of TMP in air, and are largely supported by existing spectroscopic and evolved gas analysis data. However, confirmation of the proposition, although needed from further investigation, is difficult to establish. This is simply because the identification of various changes as exotherms in the thermograms needs oxygen to be present in the system, which in turn would suppress the identity of the evolved gases (CH_2O, CH_4, CH_2 and CO) by converting them to CO, CO_2 and H_2O.

SUMMARY AND CONCLUSIONS

Trimethylol phenol has been synthesized and characterized by combined DTA–TG analyses. As it exists in uncondensed monomeric form and is available in the pure state, TMP offers itself as a model compound to establish a quantitative correlation among various steps of the curing and thermal degradation of phenol–formaldehyde resins in general.

The present study shows that the curing and decomposition of TMP with temperature quantitatively corroborate the existing views of stepwise condensation–dehydration of methylol groups to dimethylene ethers and their subsequent decomposition to methylene bridges to give a fully cured PF resin. The study confirms a clear degradation in the relative reactivities of 2,2'-, 2,4'-, and 4,4'-dimethylene ethers in their decomposition to methylene bridges. The observed order of reactivity is 4,4'->2,4'->2,2'-.

An air environment, rather than an inert one such as argon or nitrogen, has been found most satisfactory to identify these features of condensation and decomposition of PF resins.

Some valuable information on the high temperature decomposition–fragmentation of a cured PF resin is also very likely to be obtained from the combined DTA–TG thermograms of TMP. Finally, the purity and/or

identity of any methylol phenol can also be established by conventional combined DTA–TG measurements.

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