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Thermal decomposition stages of the azo linkages in novel azo phosphorus compounds. A correlative DTA study

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Abstract

Hexa amidocyclotriphosphazatriene exhibits sufficient activity to form various azo derivatives, namely, geminally bis-, tetrakis- and fully substituted phenol, catechol, resorcinol and quinol. However, the puckered structure distinguishes one of the ring phosphorus atoms with a slight upper plan location. The azo linkages associated with this phosphorus atom may therefore be strained so that they can decompose easily at a relatively low T_c and activation energy, leaving a more stable tetrakis-azo derivative. Decomposition of the latter into the geminally bis- derivative requires a considerably higher activation energy. This would imply that fully substituted azo derivatives of the present phosphorus compound might undergo decomposition via three thermally discriminated stages, effectively governed by the molecular structure. The transitions are exothermic, because the molecule transforms into a less resonating structure of less energy. Involving the azo linkage in intramolecular H-bonding, as in the case of resorcinol and quinol derivatives, would stabilize the more thermally stable hydrazone structure, which could perturb the induced mesomerism, slowing down the rate of their decomposition; this is compared to the free azo linkages of phenol and catechol derivatives with highly strained molecular structures. Various structure-dependent thermodynamic parameters are discussed.

INTRODUCTION

The mesomeric structure of the hexachlorocyclotriphosphazatriene ring initiates activity at its hexa chloro atoms so that they might undergo substitution reactions leading to geminally bis- [1], tetrakis- [2] and fully [3] substituted derivatives. In a previous thermal study [4], similar mesomeric factors have furnished activity at the hexa amino groups of hexa-amidocyclotriphosphazatriene, which facilitated a successful synthesis of the fully substituted azo phenol derivative. The effect of extended electron delocalization over the azo phenol molecule was invoked in that report [4] to substantiate discussion of the modified thermodynamic features of hexa-

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amidocyclotriphosphazatriene, because thermally induced proton mobility [5] should stabilize the more thermally stable hydrazone structure. This study has been extended in the present work to include a correlative investigation of the results of thermal decomposition of the phosphazo derivatives of fully substituted catechol, resorcinol and quinol, in addition to those partially geminally bis- and tetrakis-substituted phenols.

The aim of the present study was to extend investigation of the effects of varying mesomerism and intramolecular H-bonding on the molecular structure and the associated thermodynamic features of such novel azo derivatives, which perhaps provides a better understanding of these dependences.

EXPERIMENTAL

Materials

Hexa-amidocylotriphosphazatriene was extracted into a pure phase [4,6] distinguished by solid and melting phase transitions at 443 and 513 K respectively. A quantitative replacement of the hexa amino groups was successfully performed to form geminally bis-, tetrakis- and fully substituted azo phenols. The established method of diazotization and coupling [7] was followed to prepare these azo phenols and others, using phenol, catechol, resorcinol and quinol, all BDH, Lab. grade. The bis-azo phenol was recovered at a faster rate than the tetrakis-azo phenol which was recovered faster than fully substituted azo phosphorus compounds. Both the bis- and tetrakis-azo derivatives are distinguished by a much better solubility in polar solvents, which reflects the non-polar feature of fully substituted azo derivatives. The results of elemental analyses, particularly of carbon and hydrogen, confirmed the attempted synthesis.

Methods and equipment

The DTA of the azo phosphorus compounds was performed in air for samples weighing 0.036 g using a Shimadzu DSC TA 30 thermal analyser in the temperature range 300–1000 K, with a temperature rise of 10 K min^{-1}. The thermal data of azo resorcinol were amplified 10-fold due to its relatively low heat. The thermal data were computer-processed and were treated as described elsewhere [8].

RESULTS AND DISCUSSION

Extending the temperature range of measurement to 1000 K gave a complete thermal analysis of all the decomposition products of the present azo phosphorus compounds. The thermograms (Fig. 1) show consistently three exothermic transitions, labelled A, B and C in order of increasing T_c,

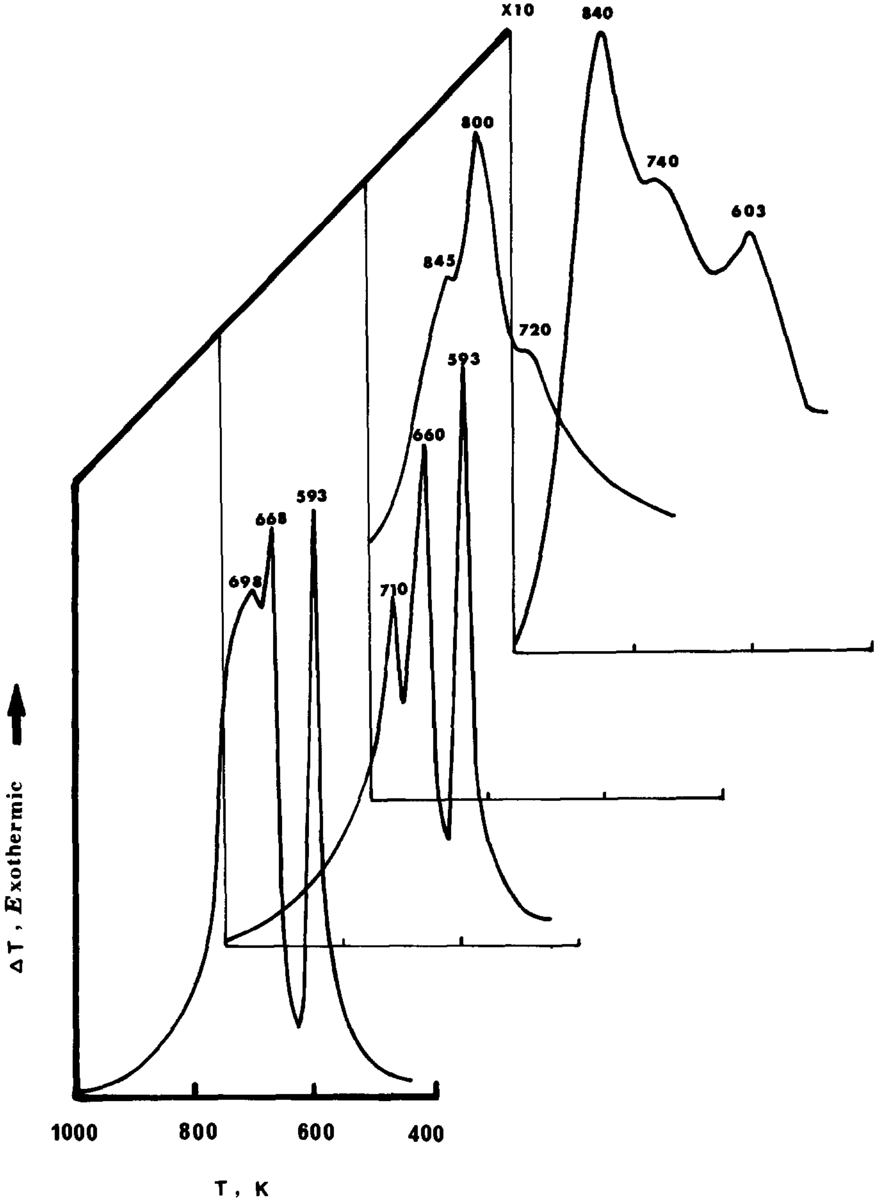

Fig. 1. Thermograms of the decomposition products of fully substituted azo derivatives. Front to back: phenol, catechol, quinol, and resorcinol.

see Table 1. This consistency is significant rather than coincident, reflecting a similar trend of thermal decomposition for the fully substituted azo derivatives of phenol, catechol, quinol and resorcinol; the latter being amplified 10-fold. It is important to stress that the decomposition products of partially substituted phenols (see later) reveal different thermograms. Decomposition of the fully substituted derivatives seems to proceed in

TABLE 1

Thermodynamic features of the three phase transitions of fully substituted azo cyclotriphosphazatriene compounds

Compound	T_c (K)	ΔH (J g^{-1})	ΔS (J g^{-1} K^{-1})	U (kJ g^{-1})	α
Azo phenol					
A	593	190.00	0.32	62.77	0.45
B	668	155.43	0.23	330.22	0.18
C	698	568.00	0.81	93.68	0.11
Azo catechol					
A	593	200.00	0.34	62.77	0.50
B	660	156.30	0.24	311.00	0.23
C	710	449.30	0.63	110.54	0.15
Azo resorcinol					
A	603	37.90	0.06	218.58	0.14
B	740	17.40	0.02	341.93	0.14
C	840	179.50	0.21	223.27	0.14
Azo quinol					
A	720	183.60	0.26	135.83	0.11
B	800	120.00	0.15	316.17	0.11
C	845	311.70	0.37	159.25	0.11

stages reflecting their formation: they form successively as geminally bis- and tetrakis- prior to their eventual formation. They decompose with three exothermic heats corresponding to the migration of the azo linkages in three groups of geminally bis-linkages. These are clearly different stages that can be followed individually. The thermogram of the partially decomposed samples after the first stage (Fig. 2, curve A) undergoes the transition shown in Fig. 2, curve B, which in turn yields the final transition (Fig. 2, curve C) on partial decomposition. The associated weight losses are 32% and 63%, which correspond to almost 1/3 and 2/3 of the sample weight respectively; the third decomposition yields 100% loss. This implies that fully substituted azo derivatives of the present phosphorus compound decompose quantitatively in three equivalent stages which are thermally discriminated due to the structural considerations under discussion.

A closer investigation of the thermogram (Fig. 1) reveals additional facts. The thermal band associated with the first stage is narrower than the latter two stages for both azo phenol and catechol. This may indicate a faster decomposition rate, perhaps because of molecular strain in these particular fully substituted azo derivatives. The relevant band of the quinol and resorcinol derivatives is quite broad, which reveals a slower rate probably the result of modified stability. There may be a structural explanation for this. Substitution in the case of quinol and resorcinol takes place in the ring ortho-position, which stabilizes the more thermally stable hydrazone structure by intramolecular H-bonding; this is at variance with the case of phenol and catechol stabilized in the more resonating azo structure.

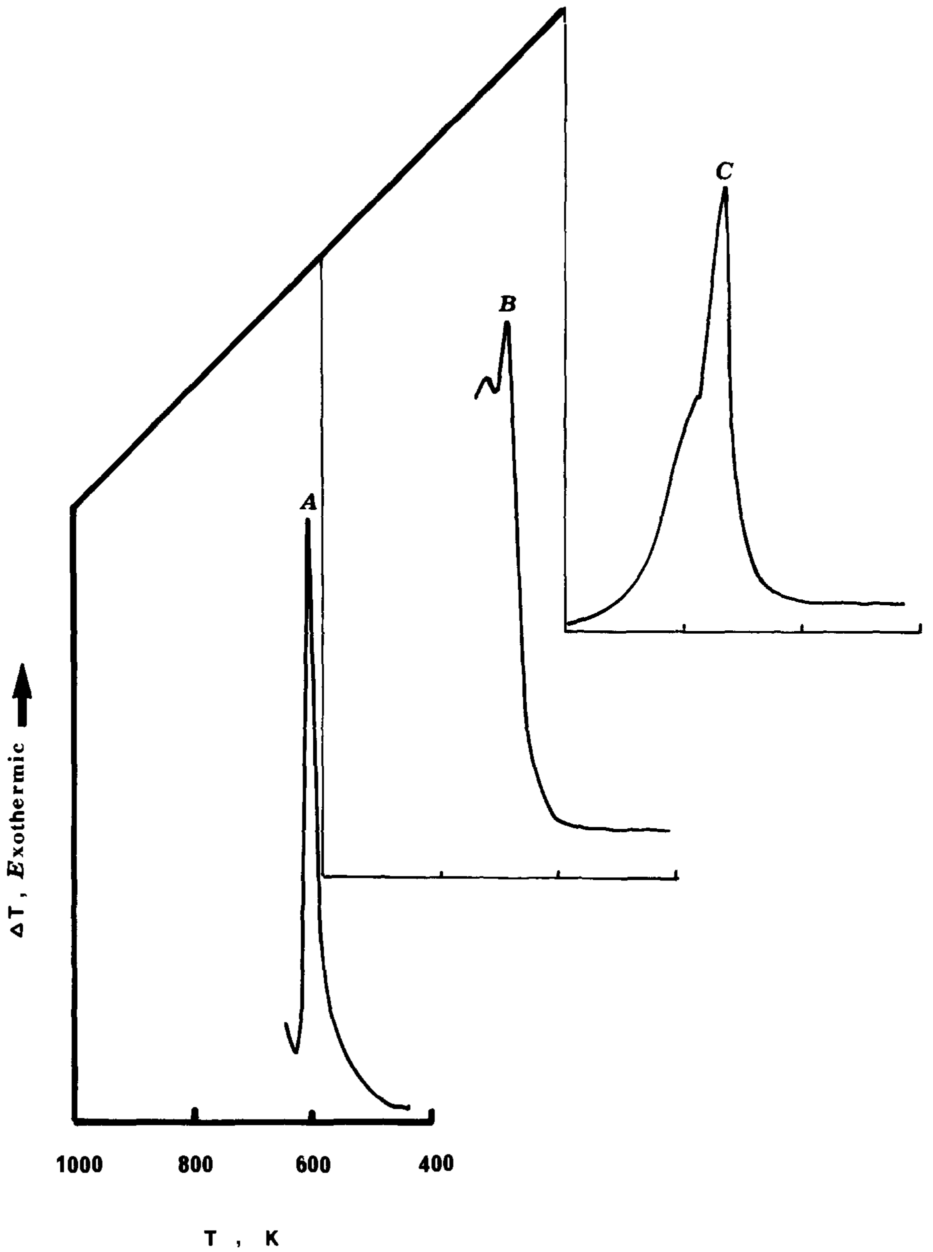

Fig. 2. Thermograms of experimentally separated decomposition products of fully substituted azo phenol.

Further strong evidence is supplied by vibrational IR spectroscopy, where the spectra of both resorcinol and quinol display a strong broad band characteristic of associated $\nu(C{=}O)$ at 1700 cm^{-1}, having no counterpart in the spectra of phenol and catechol. Involving the azo linkage in strong intramolecular H-bonding should delay the rate of their decomposition, which could explain the wide band structure of the associated thermogram of both quinol and resorcinol. Substitution in the case of phenol and catechol, however, takes place preferentially at the para position, which leaves the azo linkages free to decompose at faster rates, particularly if the molecule is strained.

Assignment of the phase transitions to the exothermic type is consistent with the structural changes involved. Such transitions must be a consequence of structure transfer into a less energetic state. Indeed, this is the case when a poly-azo phosphorus loses one or more of its azo linkages, because such a loss should bring the molecule into a less resonating structure with less energy.

Because of the complexity of the thermogram, quantitative analysis of the thermal data necessitates performing band analysis for resolving the three overlapping decomposition stages. As an approximation each of the three bands has to be considered as symmetric around T_c. The resultant data should therefore be treated as relative rather than absolute figures. The exothermic transitions are thus resolved into three bands, A, B and C (Fig. 3), of the temperature-dependent specific heats. The decomposition of azo resorcinol is distinguished by the lowest heat, which agrees with the proposal that this compound is stabilized in the less resonating hydrazone structure of less energy. The probability of such a structure is reduced for quinol because of a reduced mesomeric location, and the associated heats are therefore higher. The decompositions of phenol and catechol show the highest heats, which also agrees with the proposed azo structure of higher energy; however, involving the adjacent hydroxyls of catechol in intramolecular H-bonding reduces the extent of mesomerism. This would rank the heat of decomposition in the order phenol > catechol > quinol > resorcinol. Calculating the area under the thermogram curves as an indication of the released heats, reveals the order 52, 45, 39 and 18 cm^2 for phenol, catechol, quinol and resorcinol, respectively.

The enthalpy change of the transition ΔH is calculated based on the method of band analysis. In a common trend, the third decomposition stage (band C) shows a higher value (Table 1) than the first stage (band A) which is higher than the second stage (band B). This may indicate that the energy gap separating the excited state from the ground state for geminally bis- is higher than fully substituted which is higher than tetrakis-azo derivatives. The entropy change at T_c, ΔS, reveals a similar trend, which is understandable if it is accepted that the structural change from cyclotriphosphazatriene to the bis-azo derivative is more significant than the simple addition of one or more further azo linkages.

Estimation of the activation energy U at each transition can be achieved by plotting the logarithmic form of the relation [9]

$$\Delta C_p = (ZNU^2/RT^2)\, \mathrm{e}^{-U/RT}$$

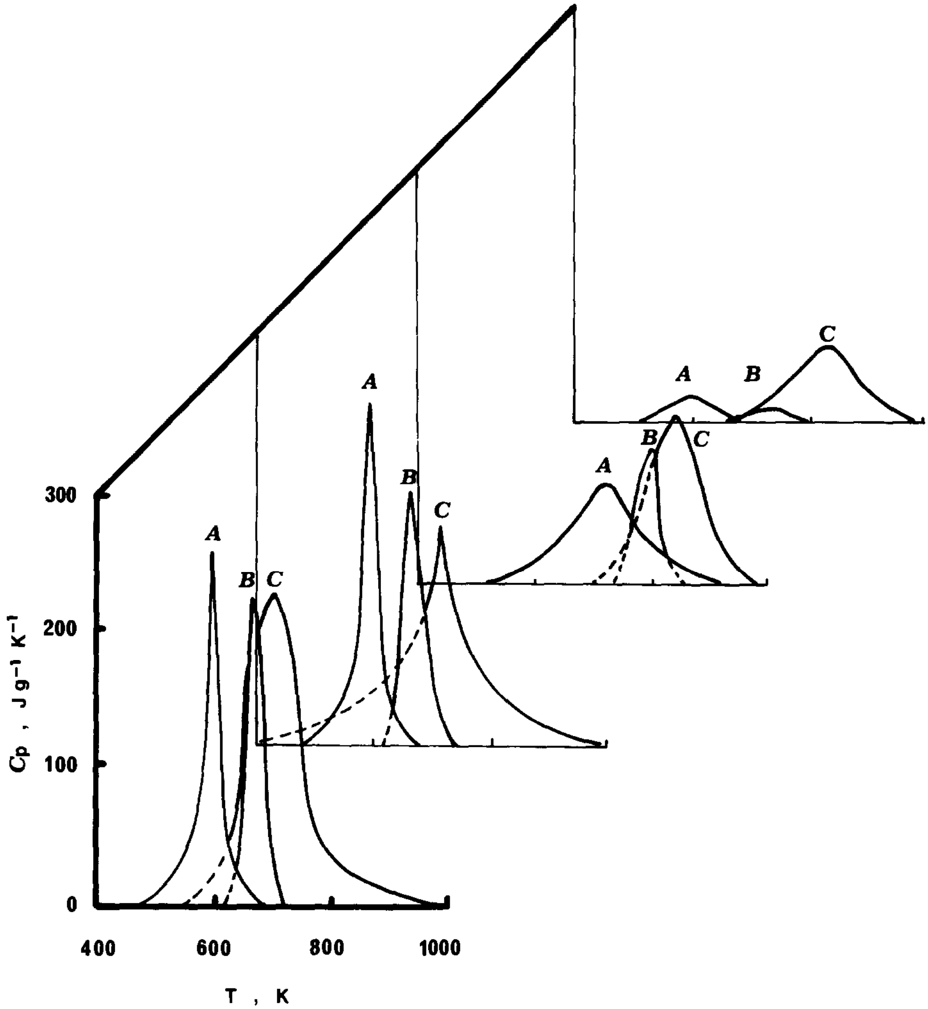

Fig. 3. The temperature-dependent C_p of the three exothermic transitions of (front to back): phenol, catechol, quinol, and resorcinol derivatives.

where Z is the coordination number, N the number of defects, R the gas constant and U the activation energy.

The slope of the linear dependence, particularly away from T_c (Fig. 4) is a measure of the activation energy; the calculated data are reported in Table 1. The activation energy is exceptionally low for the first decomposition stage of azo phenol and catechol, which agrees with other data indicative of the strained structure of these particular azo derivatives. It is generally high for the second stage of all the azo derivatives. This may imply that tetrakis-substitution results in the most stable structure among the azo phosphorus derivatives studied. This is consistent with the puckered ring structure of cyclotriphosphazatriene [10], which distinguishes one of the ring phosphorus atoms with a slightly upper plan location. This could

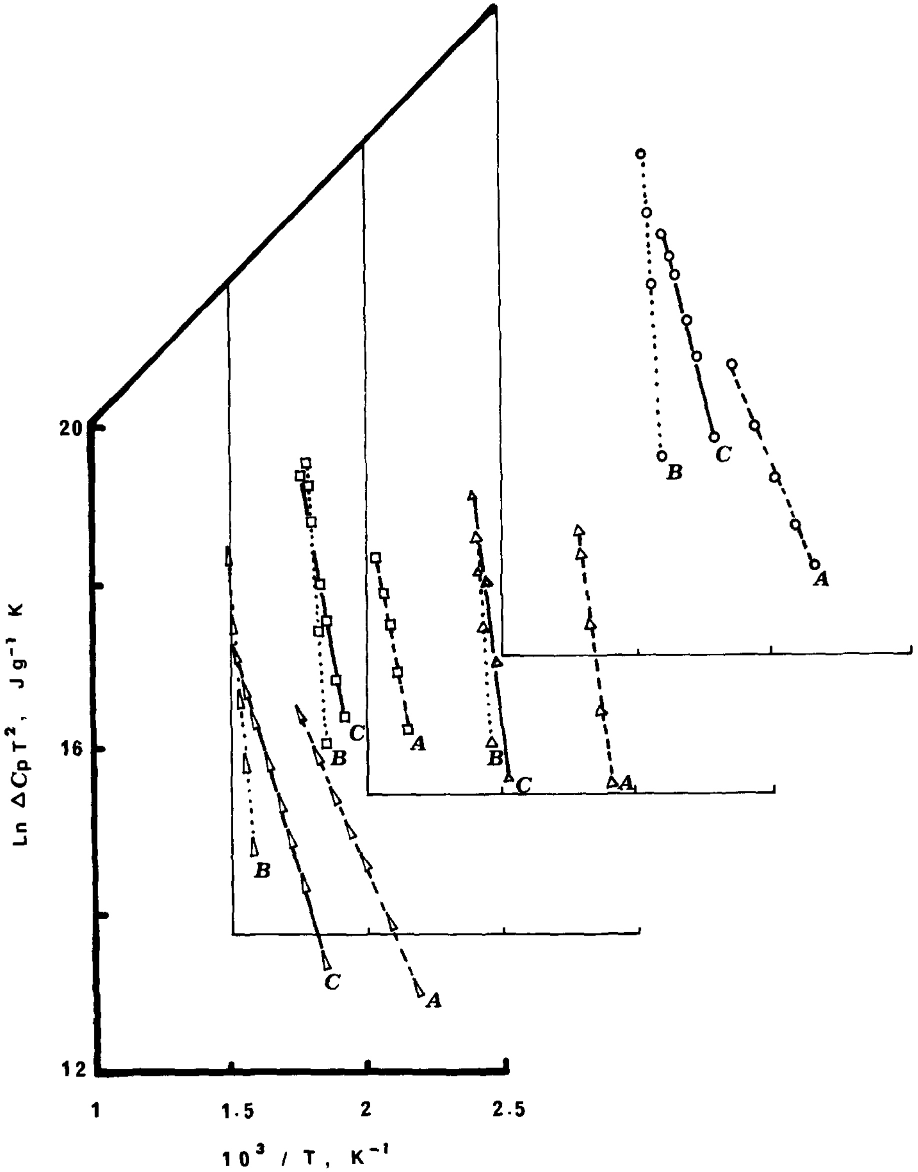

Fig. 4. Arrhenius-derived activation energy of the three transitions for (front to back) phenol, quinol, resorcinol, and catechol derivatives.

be the origin of the strained structure in fully substituted azo phenol and catechol. Decomposition of the azo linkages associated with this phosphorus atom, unless it is modified for instance by strong H-bonding, takes place with a relatively low activation energy leaving a more stable tetrakis-azo structure.

Finally, it is of interest to consider the model to which the phase transitions might be referred. The excess specific heat, ΔC_p reveals a useful

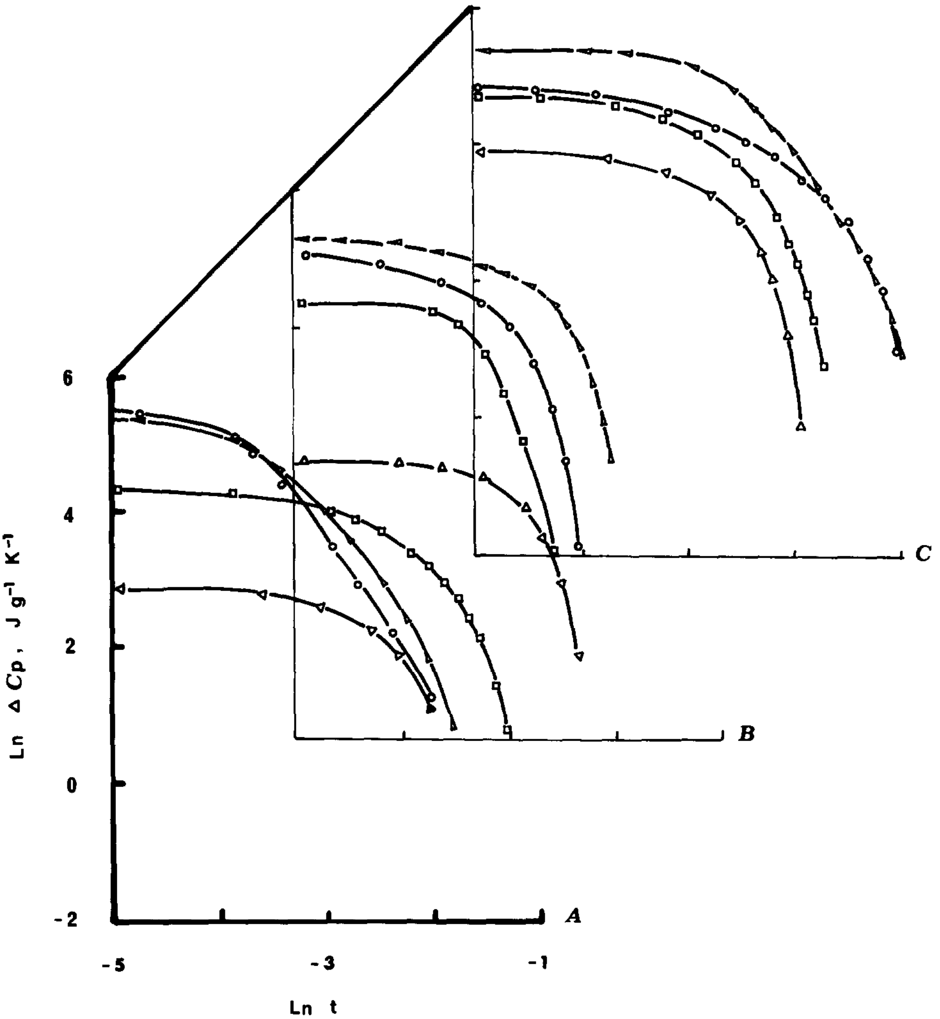

Fig. 5. Variation of the thermodynamic structural parameter, α, with the azo substituent; phenol (◄), catechol (○), resocinol (△), and quinol (□) as revealed by the three transitions A, B and C.

parameter indicative of this model α [11], when correlated with the temperature shift $t=(T-T_c)/T_c$

$$\Delta C_p = At^{-\alpha}$$

where A is a constant.

Plotting the logarithmic form of this equation, especially near T_c (Fig. 5), facilitates estimation of this parameter. The reported values (Table 1) correlate well with the 3-dimensional Ising model [12], with exceptionally higher values distinguishing the first stage for both azo phenol and catechol; this could be a consequence of disordered random distribution [13].

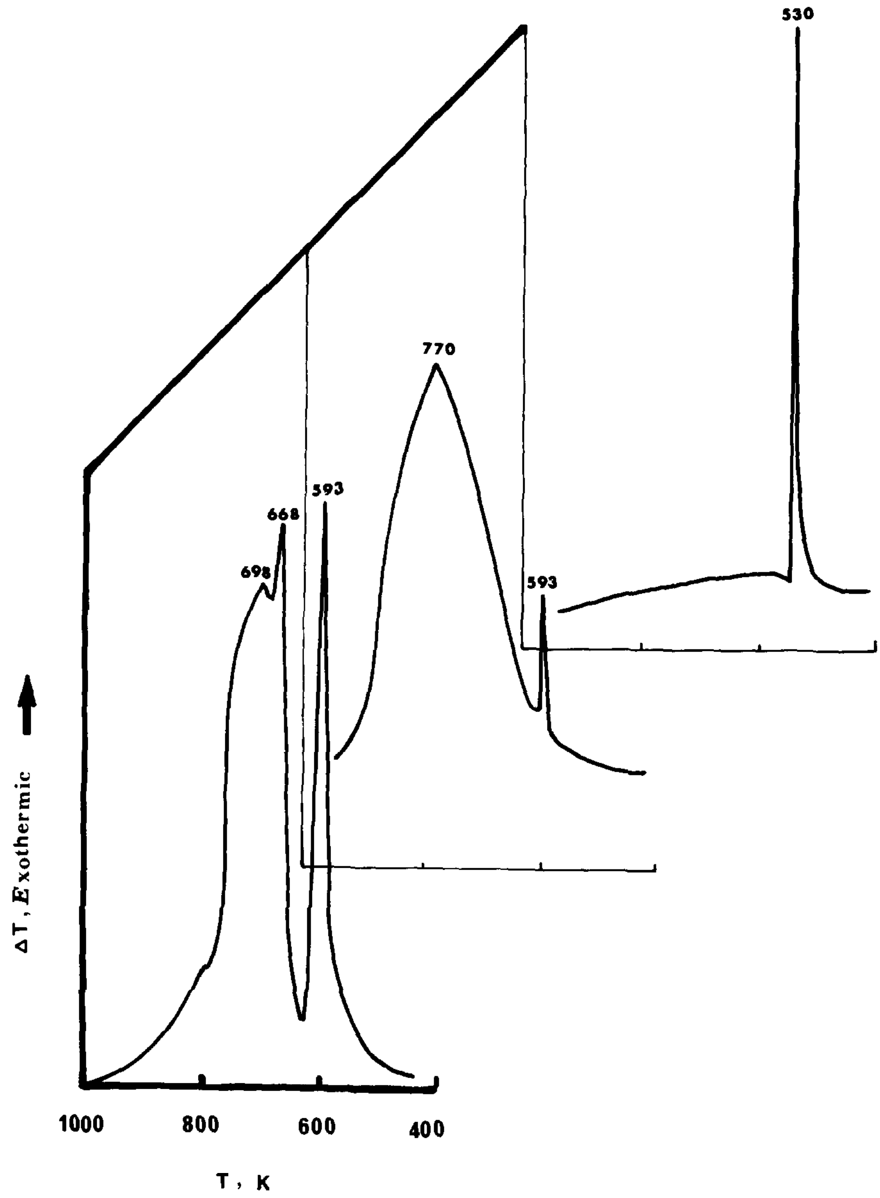

Fig. 6. Thermograms of the decomposition products of (front to back) fully substituted, tetrakis-, and geminally bis-azo phenols.

This confirms the highly strained molecular structure of these particular azo derivatives.

Figure 6 compares the DTA data of the decomposition products of geminally bis- and tetrakis- with fully substituted azo phenols. The first reveals a single exothermic phase transition, as compared to the two and three phases shown by the second and third derivatives, respectively. This gives clear experimental evidence for the proposed decomposition mechanism.

The attempted syntheses of bulkier azo derivatives were not successful. This, together with the fairly slow rate of formation of the fully substituted azo derivatives of the phosphorus compound studied, suggests the high level of strain in their molecular structure unless they are modified.

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