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Synthesis, characterization and thermal studies of 2-hydroxy-4-methoxyacetophenoneoxime–thiourea–trioxane resins

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Abstract

Resins have been synthesized by the condensation of 2-hydroxy-4-methoxyacetophenoneoxime with thiourea and trioxane in the presence of 2M HCl or H_2SO_4 as a catalyst and with varying molar proportions of reactants. The resins were characterized by elemental analyses, IR spectral study, number average molecular weight determination and viscosity. Thermal studies of the resins have been carried out to determine their mode of decomposition, apparent activation energy and the order of each thermal reaction.

INTRODUCTION

Hydroxyacetophenones and their derivatives have been condensed with formaldehyde to produce heat and light stabilizers [1,2]. Parmar et al. [3] have synthesized 2-hydroxy-4-methoxyacetophenoneoxime–formaldehyde resins in acidic media. Patel and Patel [4] have synthesized 2-hydroxy-4-methoxyacetophenoneoxime–urea–formaldehyde resins. Manavalan and Patel [5] have synthesized salicylic acid–thiourea–trioxane resins. This inspired us to report the synthesis, characterization and thermal study of 2-hydroxy-4-methoxyacetophenoneoxime (HMO)–thiourea (T)–trioxane (T′) resins.

EXPERIMENTAL

Chemicals

All the chemicals used were of AR grade. 2-Hydroxy-4-methoxyacetophenone (m.p. 52°C) was prepared by a known method [6]. 2-Hydroxy-4-

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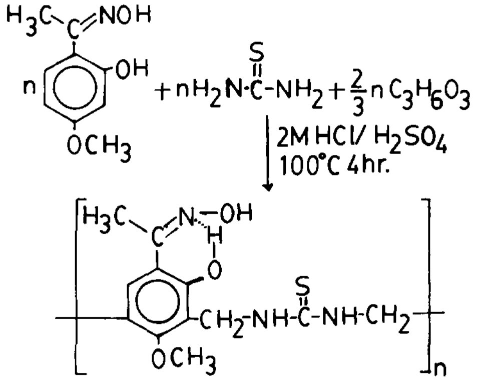
methoxyacetophenoneoxime (m.p. 130 ° C) was prepared by condensing 2-hydroxy-4-methoxyacetophenone with hydroxylamine hydrochloride in 70% ethanol.

Synthesis of resins

A mixture of 2-hydroxy-4-methoxyacetophenoneoxime (0.1 mol), thiourea (0.1 mol) and trioxane (0.2 mol) in the presence of 2M hydrochloric acid (HCl) or H_2SO_4 as a catalyst was heated in an oil bath at 100 ° C for 4 h. The separated pale yellow resin product (HMOTT′) was washed with hot water and methanol to remove unreacted monomers. The resin was purified by dissolution in 8% NaOH and reprecipitation by dropwise addition of 1 : 1 (v/v) HCl. The precipitated resin product was filtered off, washed with hot water until it was free from chloride ions and dried at 60 ° C. Different resin samples were prepared employing different molar ratios of reactants (Table 1).

Analytical methods

Microanalyses for carbon and hydrogen were carried out on a Carlo Erba Elemental Analyzer. Nitrogen was estimated by the Kjeldahl method and sulphur by the Carius method. Molecular weights of the resins were determined by non-aqueous conductometric titration in pyridine [7] and vapour pressure osmometry (VPO) using DMF as a solvent and benzil as a calibrant. The viscosity measurements were carried out in DMF at 35 ° C using an Ubbelohde viscometer. The infrared spectra in the region 4000–400 cm^{-1} were recorded in the solid state (KBr pellets) on a Perkin–Elmer 983 spectrophotometer. Thermal studies were done on a Du Pont thermal analyzer-951 at a heating rate of 10 ° C min^{-1} in air, using 5–10 mg samples.



RESULTS AND DISCUSSION

Characterization of resins

The analytical data, resin composition, intrinsic viscosity, and molecular weights are given in Table 1. All the resins are in powder form, yellow in colour and soluble in DMF, DMSO, pyridine and aq. NaOH. The resin compositions were calculated using the percentage of S in the resins. With the known % S, the percentage of thiourea repeating unit ($-CH_2-NH-CS-NH-$) (A) is given by (% $S \times 88)/32$, and the percentage of 2-hydroxy-4-methoxyacetophenoneoxime repeating unit ($-C_6H-C \cdot NOH \cdot CH_3 \cdot OH \cdot OCH_3 \cdot CH_2-$) (B) is given by ($100 - A$).

The average molecular weights of the resins determined by nonaqueous conductometric titration and by VPO are in good agreement (Table 1). The resins having higher molecular weights in the series exhibit higher intrinsic viscosity values.

IR spectral study

All the resins give rise to essentially similar IR spectra. The broad band appearing in the region 3300–3400 cm^{-1} is due to –OH and –NH stretching vibrations. The strong $\nu_{C=N}$ band at 1625 cm^{-1} and the weak band around 2600–2700 cm^{-1} indicate an intramolecular H-bond [8]. The bands in the region of 2935, 2855, 1460 and 720 cm^{-1} suggest the presence of methylene bridges in the resins [8]. The bands at 1580, 1440 and 960 cm^{-1} may be considered as composite bands of NH_2 bending, C–N stretching and C=S stretching [9]. The phenolic –OH in-plane bending and stretching are observed at 1370 cm^{-1} and 1205 cm^{-1} respectively. The band at 900 cm^{-1} indicates a pentasubstituted phenyl ring. The band at 1105 cm^{-1} indicates the N–O stretching frequency [8].

Thermal studies

The use of thermogravimetric data to evaluate kinetic parameters of solid state reactions involving weight loss has been investigated by a number of workers [10–12]. We followed the method of Broido [13]. The kinetic parameters of each decomposition step were calculated from TG curves, and are presented in Table 2. The probability that a molecule possessing energy in excess of an amount E per mole, at a temperature T, is related to the Boltzmann factor $e^{-E/RT}$, where R is the molar gas constant. The reaction rate is dependent on the product of A, which is the frequency factor, and $e^{-E/RT}$. Thus, the decomposition equation of a first-order reaction of a type $A(s) \rightarrow B(s) + C(g)$ will be $K = A\, e^{-E/RT}$. For a first order reaction, i.e. $n = 1$, this equation takes the form $\log[\ln(1/y)] = -(E/2.303R)(1/T) +$

TABLE 1

Synthesis and analytical data for resins

Resin sample	Mole ratio of reactants (% yield)	Catalyst 2M (ml)	Average molecular weight $\overline{M}_n$ by		Intrinsic viscosity $[\eta]\times10^2$ (dl g^{-1})	Analyses (%) [a]				Resin composition [a]	
			VPO	conductometric titration		C	H	N	S	A unit	B unit
HMOTT′-I	1:1:2 (54)	HCl (100)	2790	2840	7.925	51.89 (51.23)	5.30 (5.37)	14.61 (14.94)	10.94 (11.40)	0.301 (0.313)	0.699 (0.687)
HMOTT′-II	3:1:4 (57)	HCl (200)	2000	1950	5.675	58.43 (58.59)	5.67 (5.61)	9.49 (9.76)	3.54 (3.72)	0.097 (0.102)	0.903 (0.898)
HMOTT′-III	1:3:4 (45)	HCl (200)	2310	2340	6.525	47.98 (47.99)	5.15 (5.26)	16.48 (17.22)	14.39 (14.78)	0.396 (0.406)	0.604 (0.594)
HMOTT′-IV	1:1:1 (30)	HCl (50)	1580	1570	4.450	59.87 (59.70)	5.79 (5.66)	8.71 (8.98)	2.49 (2.57)	0.068 (0.071)	0.932 (0.929)
HMOTT′-V	1:1:2 (61)	H_2SO_4 (100)	2690	2750	7.475	57.93 (58.59)	5.60 (5.61)	9.31 (9.76)	3.34 (3.72)	0.092 (0.102)	0.908 (0.898)
HMOTT′-VI	3:1:4 (65)	H_2SO_4 (200)	1780	1790	5.000	59.15 (59.25)	5.82 (5.64)	8.72 (9.30)	2.88 (3.04)	0.079 (0.083)	0.921 (0.917)
HMOTT′-VII	1:3:4 (58)	H_2SO_4 (200)	1180	1180	3.325	53.64 (54.03)	5.19 (5.47)	12.44 (12.97)	8.19 (8.48)	0.225 (0.233)	0.775 (0.767)
HMOTT′-VIII	1:1:1 (44)	H_2SO_4 (50)	1500	1510	4.225	58.31 (58.59)	5.69 (5.61)	9.41 (9.76)	3.42 (3.72)	0.094 (0.102)	0.906 (0.898)

[a] Values in parentheses are those calculated.

TABLE 2

Kinetic parameters of resins

Resin sample	Stage	Temperature ranges (°C)	Weight loss (%)	Activation energy (E) (kcal mol^{-1})
HMOTT′-I	I	135–265	23.65	19.136
	II	265–475	25.26	2.952
	III	475–620	49.81	19.612
HMOTT′-II	I	140–280	18.36	18.304
	II	280–495	28.46	3.972
	III	495–650	50.96	14.872
HMOTT′-III	I	185–255	25.72	24.640
	II	255–515	27.24	2.474
	III	515–660	45.29	24.406
HMOTT′-IV	I	125–265	36.28	4.385
	II	265–495	18.40	1.525
	III	495–650	43.07	13.728
HMOTT′-V	I	135–265	20.18	11.726
	II	265–495	25.34	3.520
	III	495–640	53.04	19.830
HMOTT′-VI	I	185–275	13.64	20.800
	II	275–480	22.82	4.021
	III	480–690	55.96	14.999
HMOTT′-VII	I	160–255	23.77	21.355
	II	255–490	23.11	2.135
	III	490–660	44.61	13.074
HMOTT′-VIII	I	130–270	19.21	14.644
	II	270–460	19.74	3.178
	III	460–625	53.27	13.312

constant, where the fraction not yet decomposed (i.e. residual weight fraction) $y = (W_t - W_\alpha)/W_0 - W_\alpha)$. W_t is the weight of the substance at temperature T, W_0 is the weight of the substance at the initial stage, and W_α is the weight of residue at the end of decomposition.

TG curves are shown for selected resin samples in Fig. 1. The TG curves show three decomposition stages for all resin samples. Thermal degradation may be proposed as described earlier for phenolic resins [14,15]. Thermal degradation in the first stage may be due to the oxime and the hydroxyl group, in the second stage may be due to the methoxy group, methyl group and methylene bridges and in the third stage may be due to aromatic ring cleavage. Thermal decomposition ranges and weight loss (%) during decomposition ranges are presented in Table 2.

The plot of $\log[\ln(1/y)]$ vs. $(1/T)$ results in a straight line of slope $-E/2.303R$ (Fig. 2). The order of reaction was assumed to be one in all cases. The plots drawn according to the Broido method are found to be

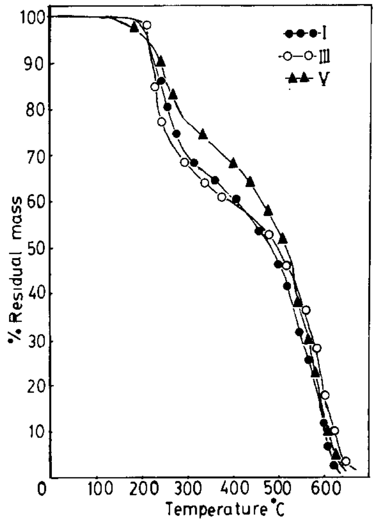


Fig. 1. TG curves for HMOTT′ resins.

linear over the entire range of decomposition, and this supplements the assumption regarding the overall order of the thermal decomposition reaction. The apparent activation energy was calculated for all the stages of decomposition (Table 2).

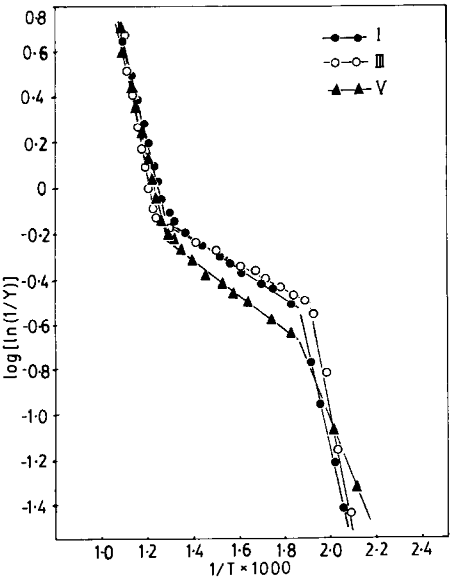


Fig. 2. Plots of log[ln(1/y)] vs. 1/T for HMOTT′ resins.

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