

THERMOCHEMICAL AND KINETIC STUDIES ON THE EFFECTS OF COBALT SALICYLATE ON THE OXIDATIVE DEGRADATION OF POLYSTYRENE

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The effect of cobalt salicylate on the oxidative degradation and ignition of polystyrene has been studied. It was found that cobalt salicylate sensitizes both the degradation and ignition of polystyrene by facilitating electron-transfer processes in the propagation step. From thermochemical and kinetic studies it was found that the cobalt ion, owing to its ability to exist in variable valence states, promotes electron transfer in the propagation step of polymer degradation, increasing the rate of propagation and consequently the overall rate. Using solid-phase thermal ignition theory, an attempt has been made to explain the sensitization of ignition by the cobalt ion.

In an earlier paper [1] we have shown that transition metal salicylates (*Msal*), when added in small quantities, sensitize the polymer ignition process and also the oxidative degradation of the polymer at 400°. In the above-mentioned paper [1] no detailed kinetic analysis was made, and only the average rate-data were presented for comparison purposes. To acquire a deeper knowledge about the mechanism of action of the metal salicylates (*Msal*), information on the thermochemical and kinetic aspects would be quite useful and rewarding. The present paper aims at fulfilling this task by considering the ignition and degradation of polystyrene (PS) containing cobalt salicylate (*Cosal*) as an additive.

Experimental

The preparation of PS, *Cosal* and PS + *Cosal* have been described elsewhere [1]. Thermogravimetric (TG) analyses were performed on a home-made TG assembly, the description of which is given elsewhere [1].

The differential thermal analysis (DTA) was carried out on an assembly described elsewhere [2]. The area under the endotherm/exotherm in the DTA curve was used to estimate the enthalpy associated with the process. The area measurements under the peaks were calibrated in units of J/degree s^{-1} , using standard substances such as tin, benzoic acid and ammonium nitrate. The calibration constant obtained was 0.1458 ± 0.0028 J/degree s^{-1} .

An assembly similar to the DTA assembly was used for ignition temperature measurements. The heating rate employed was 170°/min. At the instant of ignition, both T and ΔT display a marked deviation, as shown in the Figure. 1. The results are shown in Table 1.

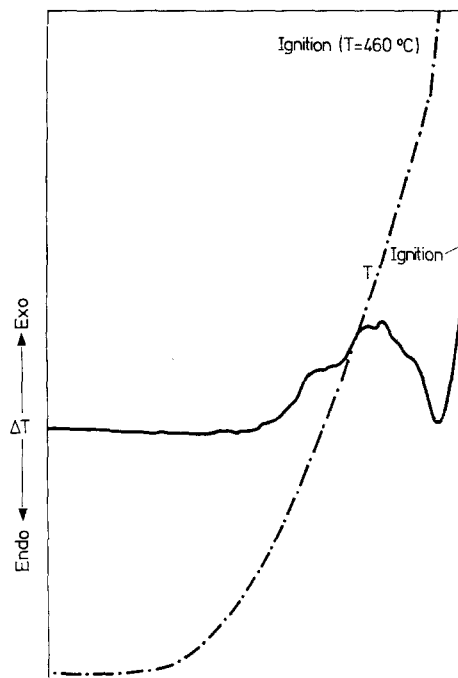


Fig. 1. A typical ignition temperature trace Sample: PS, amount: 70 mg, heating rate: 170 degree/min

Table 1

Ignition delay and ignition temperatures of PS and PS containing cobalt salicylate in various concentrations

System	Ignition delay, s	Ignition temperature, °C
PS	67.2 ± 0.6	460 ± 1
PS + Cosal (1.5%)	59.0 ± 1.3	447 ± 1
PS + Cosal (2.98%)	53.9 ± 0.9	437 ± 1
PS + Cosal (10.0%)	53.3 ± 0.6	458 ± 1

Results and discussion

The TG results on the oxidative degradation of the polymer samples at various temperatures are shown in Fig. 2. In order to obtain the order of the reaction and the rate constant, the following general equation was used:

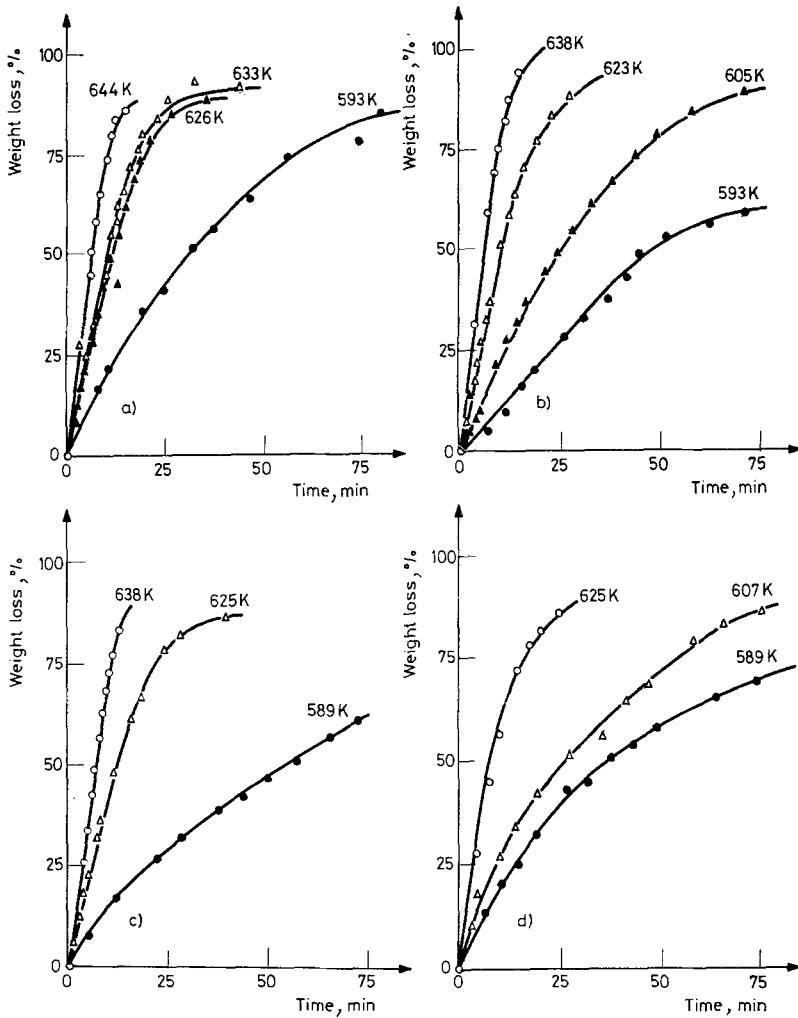


Fig. 2. TG curves of pure PS and PS containing different concentrations of Co Sal. a. PS + Co Sal (1.5 wt%); b. PS + Co Sal (2.98 wt%); c. PS + Co Sal (10.0 wt%); d. PS

$$\frac{d\alpha}{dt} = k(1 - \alpha)^n \quad (1)$$

$$\text{or, } \log (d\alpha/dt) = \log k + n \log (1 - \alpha) \quad (2)$$

A Fortran X program was developed to determine n and k from the above equation by the method of least squares. The values of k and n obtained are shown in Table 2.

Table 2

Kinetic data on the oxidative degradation of PS and PS containing cobalt salicylate in various concentrations

System	$k \times 10^4$	T, K	Order, n	Correlation coefficient
PS	0.209	589	1.42	0.981
	0.255	607	1.04	0.981
	0.944	625	1.13	0.982
PS + Cosal (1.5 %)	0.769	626	1.06	0.981
	0.778	633	0.92	0.981
	0.105	644	0.58	0.981
	0.131	593	0.41	0.982
PS + Cosal (2.98 %)	0.866	623	1.03	0.981
	0.145	588	1.20	0.982
	0.125	638	0.61	0.981
	0.258	605	0.74	0.981
PS + Cosal (10 %)	0.144	589	1.17	0.980
	0.830	638	0.41	0.982
	0.583	625	1.00	0.981

An assembly described earlier [1] was used to measure the ignition delay (ID) of the various samples.

It can be seen from Table 2 that, though there are some values of n that are quite off, the majority of the values fall around unity, and hence the order of the reaction can be taken as unity. This, in fact, lends strong support to the general belief that the degradation of vinyl polymers generally follows 1st-order kinetics [3].

Considering the order of the reaction as unity, the rate constants were calculated (i.e. k corresponding to $n = 1$). It is interesting to note here (Table 3) that when k is calculated taking the order as unity, the correlation coefficient is -0.99 in almost all cases, compared to 0.98 obtained earlier (Table 2), where the order was not taken as unity.

The activation energies (E) were obtained by plotting $\ln k$ vs, $1/T$ and results are presented in Table 3. E varies in the range 120–160 kJ/mole for the various polymer systems studied.

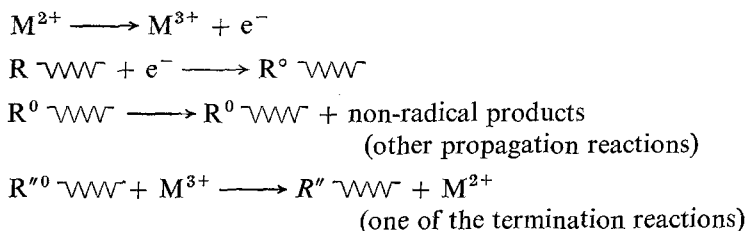
By considering the average rate for $\alpha = 0.1 - 0.6$, the Jacobs–Kureishy method [4] was also used to obtain E by the two methods. These data too are shown in Table 3. It is seen that the E agreement between the two methods is quite good. Although the E values differ from sample to sample, they are not too far from 125 kJ/mole. In an earlier paper [5] it was shown that E for the oxidative degradation of PS is 125 kJ/mole, and the present work supports that observation. An E of 125 kJ/mole for the oxidative degradation of PS has also been reported by Knight [6]. In an earlier paper [7] it was shown that the E corresponds to the initiation step to

Table 3

Kinetic data on the oxidative degradation of PS and PS containing cobalt salicylate in various concentrations for $n = 1$ (Also included are the activation energies obtained by the Jacobs-Kureishy method [4])

System	$k \times 10^4, s^{-1}$	T, K	Correlation coefficient	Activation energy, kJ/mole	Activation energy by J-K method, kJ/mole
PS	2.133	589	-0.994	163 ± 0.5	134 ± 0.5
	4.267	607	-0.991		
	14.717	625	-0.997		
PS + <i>Cosal</i> (1.5%)	3.517	593	-0.988	121 ± 0.5	121 ± 0.5
	12.033	626	-0.998		
	14.433	633	-0.996		
	25.717	644	-0.995		
PS + <i>Cosal</i> (2.98%)	2.250	588	-0.998	167 ± 0.5	155 ± 0.5
	5.833	605	-0.977		
	13.867	623	-0.999		
	33.883	638	-0.984		
PS + <i>Cosal</i> (10%)	2.067	589	-0.999	151 ± 0.5	142 ± 0.5
	9.800	625	-0.994		
	24.850	635	-0.989		

form macroradicals. Since the *Msal*'s do not change the E , this suggests that the *Msal*'s do not affect the polymer degradation in the initiation step, but act in the propagation step, as has been proposed previously [1]. The mechanism of the metal ion catalysed polymer degradation can therefore be written as follows:



Thus, the *Msal*'s accelerate the polymer degradation by accelerating the propagation reactions by e^- transfer.

Attention may be drawn to Table 4, where the enthalpy changes during polymer oxidative degradation in the presence and absence of *Cosal*, together with the heat released by *Cosal* itself, are presented. Column 2 of Table 4 gives the experimental enthalpy values of PS, *Cosal* and PS + *Cosal*, and column 3 of the same Table gives

Table 4

Experimental and calculated enthalpy values of PS, *Cosal* and PS containing various concentrations of *Cosal*

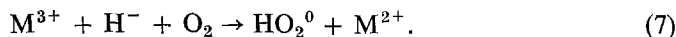
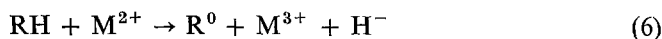
System	Enthalpy, J/g	
	Experimental	Calculated
PS	+ 461	—
<i>Cosal</i>	— 5438	—
PS + <i>Cosal</i> (1.5%)	— 379	+373
PS + <i>Cosal</i> (2.98%)	— 621	+286
PS + <i>Cosal</i> (10%)	— 1177	— 129

the corresponding calculated enthalpy values, wherever appropriate. These values for PS + *Cosal* mixtures were obtained from the heats of degradation of PS and *Cosal* and the fractions of the components present in the mixture. It may be seen that the experimental enthalpy changes are highly exothermic compared to the calculated values for the mixture, where even endotherms are expected for the first two compositions. This therefore strongly suggests that the *Msal*'s, besides increasing the rate of oxidative degradation of PS, bring about an enormous increase in the extent of oxidation, so that a large amount of heat is liberated during degradation.

The extent of oxidation is dependent on the extent of hydroperoxide formation as follows:



Of these three reactions, (4) and (5) do not need any aid from the *Msal*'s for quantitative conversion. Hence, the *Msal*'s most probably act in (5) to produce more of the free radicals, by increasing the extent of decomposition of RH. A possible mechanism for this may be as follows:



If these two reactions are more feasible than the decomposition of RH by itself, then the extents of formation of R^0 and HO_2^0 will be higher. Consequently, more ROOH will be formed and hence there will be an increase in the heat of the oxidative degradation.

Modelling studies of polymer ignition process has not received due attention in the past, and many important problems remain unsolved. The solid-phase thermal model [8] considers the heat conduction in the solid such that the ignition is con-

trolled by the temperature rise in the solid phase, and it does not consider any gas-phase reactions. In fact, this model has been widely used for propellants and explosives, where exothermic heat is produced inside the solid when it is heated. In view of the fact that the additive gives out exothermic heat during polymer oxidative degradation, an attempt was made to describe the process of polymer ignition in the present case using this equation.

The solid-phase thermal model is given as follows:

$$\tau^{1/2} = \frac{K}{2 \dot{Q}} (T'_{ig} - T_0) \left(\frac{\pi}{\alpha} \right)^{1/2}. \quad (8)$$

K is the thermal conductivity of the system, T'_{ig} the ignition temperature, τ the ignition delay, T_0 the ambient temperature, α the thermal diffusivity and \dot{Q} the thermal heat flux.

The thermal heat flux can be given by the following equation:

$$Q^\circ = \Delta H' k' C_0. \quad (9)$$

Where, $\Delta H'$ is the heat of reaction, k' the rate constant and C_0 the concentration. (As the order was observed to be unity, the exponent of C_0 has been taken as unity in the above equation.)

Using (8) and (9), we get

$$\tau'^{1/2} = \frac{K}{2 \Delta H' k' C_0} (T'_{ig} - T_0) \left(\frac{\pi}{\alpha} \right)^{1/2}. \quad (10)$$

In the presence of *Msal*, the polymer ignition is given by the following equation (the initial concentration of the polymer is maintained constant and it is assumed that the small quantity of the additive will not change α):

$$\tau''^{1/2} = \frac{K}{2 \Delta H'' k'' C_0} (T''_{ig} - T_0) \left(\frac{\pi}{\alpha} \right)^{1/2}. \quad (11)$$

From (10) and (11), we get

$$\frac{\tau'^{1/2}}{\tau''^{1/2}} = \frac{\Delta H'' k''}{\Delta H' k'} \frac{(T'_{ig} - T_0)}{(T''_{ig} - T_0)}. \quad (12)$$

This equation gives the ratio of the ID's of two systems.

The necessary ΔH values from Table 4 were substituted into the above equation.

When the various parameters are substituted into the above equation, we get the ratio of the calculated ID's from equation (12) for PS + *Cosal* (1.5%) and PS + *Cosal* (2.98%) to be 1.92, whereas the experimentally determined ratio is 1.05.

This shows that the above equation predicts the ID qualitatively but not quantitatively. The reason for this may be that the solid-phase ignition model is not entire-

ly applicable for polymer ignition. In other words, the ignition is governed by gas-phase reactions too. In the above calculations, pure PS was not considered for the calculations, as it does not give any exotherm during degradation.

References

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ZUSAMMENFASSUNG — Die Wirkung von Kobaltsalicylat auf den oxydativen Abbau und die Entzündung von Polystyrol wurde untersucht. Es wurde festgestellt, daß Kobaltsalicylat sowohl den Abbau als auch die Entzündung des Polystyrols durch Erleichterung von Elektronentransferprozessen im Kettenfortpflanzungsschritt begünstigt. Thermochemische und kinetische Untersuchungen ergeben, daß das Kobaltion infolge seiner Fähigkeit, in mehreren Valenzstufen aufzutreten, den Elektronentransfer im Kettenfortpflanzungsschritt erleichtert wodurch die Geschwindigkeit der Kettenfortpflanzung und damit die Geschwindigkeit des Gesamtprozesses erhöht wird. Basierend auf der Theorie der thermischen Festphasenentzündung wird ein Versuch unternommen, Erleichterung der Entzündung durch Kobaltionen zu erklären.

Резюме — Изучено влияние салицилата кобальта на окислительное разложение и воспламенение полистирола. Найдено, что салицилат кобальта сенсibiliзирует разложение и воспламенение полистирола, облегчая процессы электронного переноса в стадии роста цепи. Из термохимических и кинетических исследований установлено, что ион кобальта, вследствие способности существовать в различных валентных состояниях, способствует электронному переносу в стадии роста цепи распада полимера, увеличивая скорость роста и тем самым увеличивает суммарную скорость. Используя теорию твердофазного термического воспламенения, предпринята попытка объяснить сенсibiliзирующее действие иона кобальта.