

THERMOANALYTICAL STUDIES OF RUBBER OXIDATION CATALYZED BY METALLIC IONS*

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ABSTRACT

The effects of several metallic ions on the oxidation of natural rubber were studied by differential scanning calorimetry (DSC). The activation energy of oxidation was evaluated from DSC curves. Cobalt, manganese, iron and copper ions decreased the activation energy of oxidation. Nickel, zinc and tin ions did not affect the activation energy. The effective ions are those which are able to undergo one-electron transfer redox reaction with hydroperoxide. Based on the activation energy values, the catalytic activities of metallic ions are: $\text{Co} > \text{Mn} > \text{Cu} \approx \text{Fe} \gg \text{Ni} \approx \text{Zn} \approx \text{Sn}$.

INTRODUCTION

The catalytic effects of metallic ions on the oxidation of rubber have been studied for many decades. For example, Chovin¹ reported the activities of various organic derivatives of copper, iron, cobalt and manganese on the oxidation of vulcanized rubber. Leyland and Stafford² studied the effects of metallic salts on the oxidation of both raw and vulcanized natural rubber, styrene-butadiene rubber and nitrile rubber. Lee and co-workers³ studied the effects of ten metallic stearates on the oxidation of nine types of synthetic rubbers. Oxygen absorption measurements were used in these studies as well as in many other oxidation studies.

Recently, thermoanalytical techniques have been used to study rubber oxidation^{4–8}. The position of the oxidation peak^{4, 5} and the heat change during oxidation⁶ as evaluated from thermoanalytical studies were considered useful in evaluating the effectiveness of antioxidants. Based on the position of the oxidation exotherm, May and Bsharah⁷ evaluated the catalytic activities of metallic ions on the oxidation of styrene-butadiene rubber and also the deactivation of ions by antioxidants.

Previous work⁸ showed that the activation energy of oxidation evaluated from thermoanalytical studies provided a reasonable estimation of the effectiveness of antioxidants. The purpose of this work is to investigate the effects of several metallic

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ions on the activation energy of oxidation of natural rubber and to demonstrate the applicability of activation energy as a means to measure the catalytic activities of metallic ions.

EXPERIMENTAL

Materials. Natural rubber of pale creep grade was used. The naphthenates of cobalt, copper, iron, manganese, nickel, tin and zinc were obtained from K and K Laboratories Inc. The metallic naphthenates were used as received.

Equipment. A Perkin-Elmer DSC-1B differential scanning calorimeter was used. The instrument was calibrated according to the manufacturer's operating manual. The instrument was purged with oxygen at a flow rate of 20 ml min⁻¹ during operation. The samples were scanned with the following heating rates: 2, 4, 8, 16, 32 and 64 K min⁻¹.

Sample preparation. Natural rubber was first extracted with acetone for 24 h to remove natural antioxidant. It was further purified by solution in benzene, followed by precipitation in methanol.

To prepare samples for DSC tests, a small amount of metallic naphthenate was first weighed and dissolved in benzene. The appropriate amount of purified rubber was also weighed and dissolved in benzene to make a 2% solution and the two solutions thoroughly mixed. A drop or two of the solution was placed in the sample pan and allowed to dry, forming a thin film with a thickness of about 10⁻³ cm. In this manner, a good contact between sample and sample pan is ensured. Furthermore, by employing a thin film of this thickness, the rate of oxidation will not be diffusion controlled⁹.

Evaluation of activation energy. The activation energy of oxidation E was evaluated by using Kissinger's method¹⁰

$$d \ln(r/T_p^2)/d(1/T_p) = -E/R$$

where T_p is the oxidation peak temperature and r is the heating rate. E was calculated from the plot of $\ln(r/T_p^2)$ versus $1/T_p$ using least-squares method. Kissinger's method was successfully used in the evaluation of activation energy of oxidative thermal degradation of plastics¹¹.

RESULTS AND DISCUSSION

The DSC curves of purified natural rubber containing 0.1% of metallic naphthenates scanned with a heating rate of 16 K min⁻¹ are shown in Fig. 1. Oxidation exotherms were observed between 420 and 470 K. The position of the oxidation peak (T_p) was reproducible and seldom varied by more than one or two degrees. The addition of tin, zinc and nickel ions did not affect the shape and position of the oxidation exotherm of natural rubber. For samples containing cobalt, iron and copper ions, the exotherms were slightly broadened and T_p were 3-5 degrees lower as

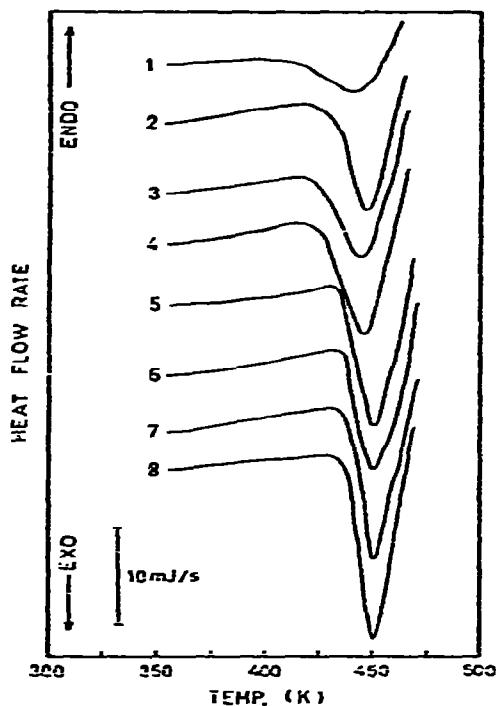


Fig. 1. DSC curves of natural rubber containing 0.1% of metallic naphthenate. (1) manganese (sample weight: 0.47 mg); (2) cobalt (sample weight: 0.66 mg); (3) iron (sample weight: 0.47 mg); (4) copper (sample weight: 0.63 mg); (5) tin (sample weight: 0.56 mg); (6) zinc (sample weight: 0.57 mg); (7) nickel (sample weight: 0.50 mg); (8) blank (sample weight: 0.56 mg).

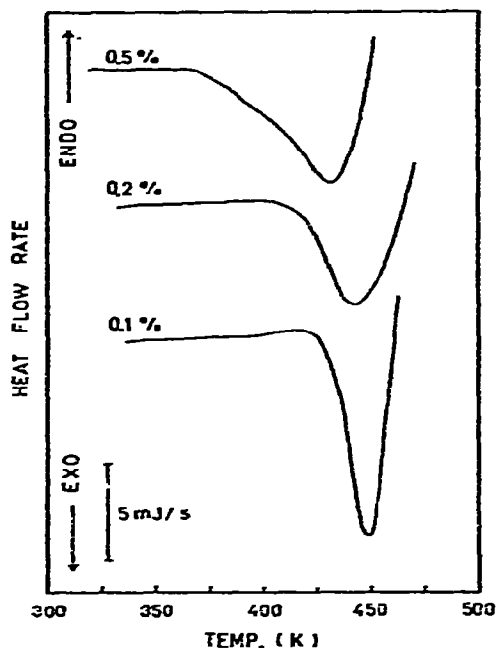


Fig. 2. DSC curves of natural rubber containing various amounts of cobalt naphthenate.

compared with the blank sample. The addition of manganese ion produced a broad and shallow exotherm with T_p at 10 degrees lower.

The DSC curves of samples containing 0.2% and 0.5% of metallic naphthenates other than cobalt naphthenate were essentially identical to the corresponding 0.1% samples without noticeable change in the shape and position of the exotherm. However, increasing amounts of cobalt ion affected the oxidation exotherm as shown in Fig. 2. The exotherm became broadened and T_p decreased.

The Kissinger plots of samples containing 0.1% of metallic naphthenates are shown in Fig. 3. Straight lines with correlation coefficients better than -0.99 were obtained in all cases. The T_p values of various samples were quite similar at faster heating rates while a substantial difference in T_p was observed at slower heating rates. Therefore a slow heating rate must be employed if T_p is used as the criterion as proposed by May and Bsharah⁷.

The activation energies of oxidation of various samples evaluated from the Kissinger plots are shown in Table 1. The activation energies of acetone extracted and purified natural rubber were 71.5 and 70.7 kJ mol^{-1} respectively which were lower than the previously reported value of 83.5 kJ mol^{-1} for acetone extracted natural

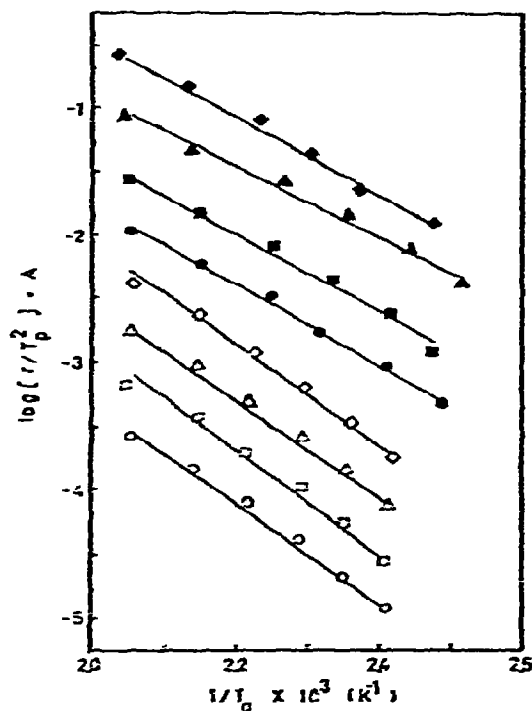


Fig. 3. Kissinger plots of natural rubber containing 0.1% of metallic naphthenate. \blacklozenge cobalt ($A = 3.0$); \blacksquare iron ($A = 2.0$); \diamond tin ($A = 1.2$); \square nickel ($A = 0.4$); \blacktriangle manganese ($A = 2.5$); \bullet copper ($A = 1.6$); \triangle zinc ($A = 0.8$); \circ blank ($A = 0$).

TABLE I

ACTIVATION ENERGY OF OXIDATION OF NATURAL RUBBER CONTAINING VARIOUS AMOUNTS OF METALLIC NAPHTHENATE

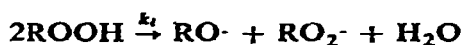
	Activation energy (kJ mol^{-1})		
	0.1%	0.2%	0.5%
cobalt	59.9	50.5	41.5
manganese	51.4	53.5	51.7
iron	59.4	56.8	61.5
copper	60.2	59.7	60.3
nickel	72.5	74.1	72.2
tin	71.6	72.1	76.2
zinc	72.7	71.5	74.2
blank: 70.7 kJ mol^{-1}			

rubber⁵. The discrepancy was not due to experimental error but rather to the use of different batches of natural rubber in the two separate studies as repeated experiments on purified natural rubber gave similar activation energy values. Since the same batch of rubber was used throughout the present study, the activation energy values were

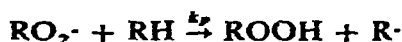
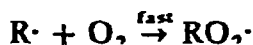
considered to be valid for comparison purposes. With the exception of cobalt naphthenate, the activation energy appeared to be independent of the amount of metallic naphthenate added.

The oxidation of rubber is considered to proceed according to the following reaction scheme¹²⁻¹⁵

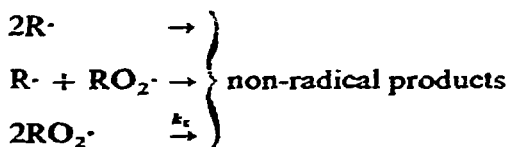
Initiation:



Propagation:



Termination:



Under steady-state condition, the rate of oxidation is given by

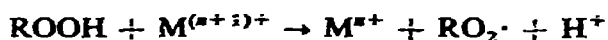
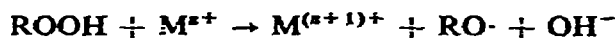
$$-\frac{d[\text{O}_2]}{dt} = k_p[\text{RH}]R_i^{\frac{1}{2}}/k_t^{\frac{1}{2}}$$

Where R_i is the rate of the initiation step. The overall activation energy E of oxidation is then given by

$$E = E_p + \frac{1}{2}E_i - \frac{1}{2}E_t$$

Where E_i , E_p and E_t are the activation energies for the initiation, propagation and termination step respectively.

Metallic ions were considered to react with hydroperoxide through one-electron transfer redox reactions as shown below^{16, 17}

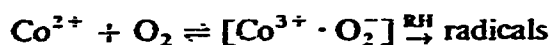


The sum of the two equations is equivalent to the initiation step as mentioned earlier. The decomposition of hydroperoxide is therefore catalyzed by metallic ions and the activation energy of the initiation step E_i is reduced, resulting in a reduction of the overall activation energy E . Hence the activation energy values should provide a means to measure the relative catalytic activities of various metallic ions.

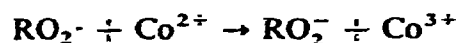
Based on the activation energies as given in Table 1, cobalt and manganese ions are very effective catalysts, followed by copper and iron ions. The reduction in activation energy amounts to 10 to 30 kJ mol⁻¹, corresponding to a decrease in E_i by

20 to 60 kJ mol⁻¹. The activation energy for the decomposition of organic hydroperoxide is about 120 kJ mol⁻¹. Thus the addition of an effective catalyst can reduce the activation energy by one-half. The activation energy values also indicate that tin, zinc and nickel are ineffective, in agreement with the results of Lee and co-workers³.

The appreciable decrease in activation energy with increasing amount of cobalt naphthenate indicated that the cobalt ion catalyzed oxidation of rubber could be very complex. Reactions other than the catalysis of the decomposition of hydroperoxide were possible. Several reactions have been suggested as shown below^{17, 18}



Moreover, cobalt ion was reported to inhibit oxidation at high concentration and the following reaction has been suggested¹⁸⁻²¹



Similar inhibiting effects of manganese and copper ions at high concentration have also been reported¹⁸⁻²⁰.

Nonetheless, based on the activation energy values, the relative catalytic activities of metallic ions are: Co > Mn > Cu ≈ Fe ≫ Ni ≈ Zn ≈ Sn. The order of activity of the effective ions agrees with the results of Lee and co-workers³ as well as Mayo and co-workers²² based on oxygen absorption measurement. Therefore the activation energy evaluated from thermoanalytical studies does provide a reliable means to evaluate the catalytic activity of metallic ion. The present study also substantiates the conclusions of Lee and co-workers³ that: (1) those metallic ions having adjacent stable oxidation states such as copper, iron, cobalt and manganese ions are catalytically active; (2) those ions having stable higher oxidation states but requiring two-electron transfer such as tin and lead ions are inactive; (3) those ions without stable higher oxidation states such as zinc ion are also inactive.

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