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Effect of metal oxides on the kinetics of thermal oxidative degradation of nylon-6

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Abstract

The rate constants and kinetic parameters for the thermal oxidative degradation of nylon-6 in the presence of metal oxides show the existence of a true kinetic compensation effect. This pattern of behaviour amongst metal oxides in the oxdiative degradation of nylon-6 has been linked to the higher oxidation state. The behaviour suggests that the reaction follows a redox or electron transfer mechanism due to tunnelling of electrons.

INTRODUCTION

Comparisons of the thermal oxidative stabilities of vinyl polymers and polybutadiene in the presence of metal oxides and other compounds have been made by many workers [1,2]. The surface area of the metal oxides has been recognized as a factor of considerable importance in the thermal decompositon reactions [3]. A reduction of the induction period is exhibited by polymers containing many metal oxides, but alkali metal oxides have been found to be inactive. Studies of the catalytic activity of copper(II) and copper(I) oxides on the oxidation of polypropylene suggest that copper(I) oxide is the more active because it is a p-type semconductor [2], and it is well established that p-type semiconductors are the most effective catalyst for the oxidation of hydrocarbons. The oxidative degradation of polymers has not been systematically studied and the precise mechanism of their thermal oxidative degradation in the presence of oxides remains unknown.

In this paper we consider the kinetic compensation effect (c.e.) as a common feature in the thermal oxidative degradation of nylon-6 in the presence of metal oxides. With the c.e. as a basis, we have tried to interpret the influence of metal oxides on the thermal oxidative degradation of nylon-6.

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MATERIALS

Commercial moulding grade nylon-6 was obtained from Garware Nylon Ltd., Pune and was purified by solvent–non-solvent precipitation (*m*-cresol and ethanol).

The sources and physical properties of the oxides are listed in Table 1.

TABLE 1

Sources and physical properties of metal oxides[a]

Metal oxide	Purity/%	Source	Type of semiconductor	Width of forbidden zone/eV
MoO_3	99	Sisco-Chem	n or p	2.9
Cu_2O	98	Sisco-Chem	p	1.9
Sb_2O_3	99	Lab-Chem	p	4.2
Cr_2O_3	–	Robert Johnson	n or p	1.9
Fe_2O_3	98	Sarabhai	n	1.9
ZrO_2	–	Sisco-Chem	n	2.3
V_2O_5	–	Sisco-Chem	n	2.1
Al_2O_3	–	–	n	7.3
TiO_2	98	Sarabhai	n	3.1
ZnO	99.5	BDH	n	3.3
CeO_2	–	Sisco-Chem	n	1.3
CuO	96	Sarabhai	n or p	1.4
MnO_2	–	BDH	n	0.3 or 0.6
SnO_2	–	Sisco-Chem	n	3.8
Ni_2O_3	–	–	–	–
PbO	98	BDH	–	–

[a] O.V. Krylov, Catalysis by Non-metals — Rules for Catalyst Selection, Academic Press, London, 1970, pp. 247–258.

Sample preparation

Powdered nylon-6 was mixed with metal oxide in an arbitrarily chosen ratio of 5:1 (5 parts nylon-6 and 1 part metal oxide by mass). After mixing, the mixture was further ground in an electrical vibrator in order to obtain an intimate mixture of nylon-6 and the metal oxide. The resulting mixture was used in the TGA studies.

EXPERIMENTAL

Thermogravimetric measurements

Thermogravimetric analysis was carried out in the presence of static air. About 50 mg of sample was placed in a platinum crucible and the mass loss was recorded as a function of temperature. The heating rate was maintained at 4 K min^{-1}.

RESULTS AND DISCUSSION

The effect of metal oxides on the thermal oxidative degrading of nylon-6 was examined by heating the polymer and metal oxide mixture at a constant rate in a thermobalance in static air. The TG curve for a representative sample of nylon-6 mixed with CuO and Cu_2O is shown in Fig. 1. In all cases, there was no initial mass increase on heating and the degradation occurred in a single step decomposition. However, it is interesting to note from the TG curve that the amount of residue was the same in all cases except for CuO, owing to the decomposition of CuO to Cu_2O at elevated temperature as reported by Hansen et al. [2].

From the TG data, the rate of mass loss as a function of furnace tempeature was calculated and is plotted in Fig. 2. From Fig. 2, the temperature at which the rate of mass loss reached a maximum was determined, and is recorded in Table 2. This temperature T_{max} was taken to be a measure of thermal stability; from Table 2 it can be seen that the metal oxides of V(V), Zr(IV), Ti(IV), Fe(III), Cu(II), Mn(IV), Ni(III), Mo(VI) and Ce(IV) lowered the thermal stability of nylon-6. These transition metals are in their highest oxidation state and T_{max} is less than that for pure nylon-6, i.e. 480°C. Mixtures of nylon-6 and metal oxides such as those of Sb(III), Pb(II), Zn(II), Cr(III) and Sn(IV) have T_{max} values higher than that of nylon-6. These latter metal oxides stabilize the polymer. From Table 1 it can be noted that metal oxides which are in the first category are all n-type semiconductors. Cu(II) and those in the latter category are either p-type or n-type. The oxidative degradation of nylon-6 is largely independent of semiconductor type.

In order to understand the collective behaviour or the dependence of thermal oxidative degradation on the bulk properties of metal oxides, TG

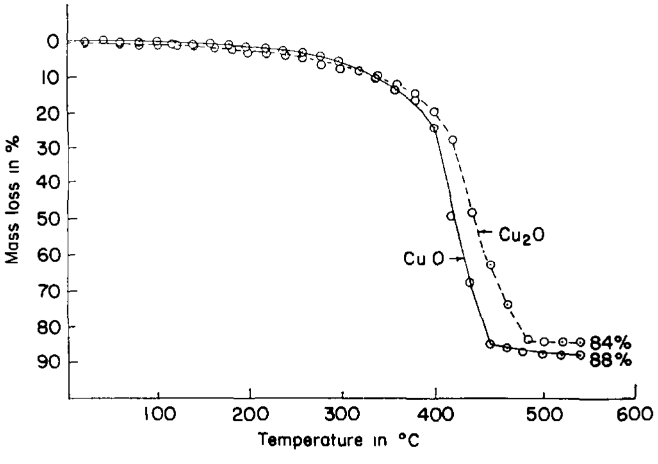

Fig. 1. TG curve of nylon-6 mixed with Cu_2O; CuO.

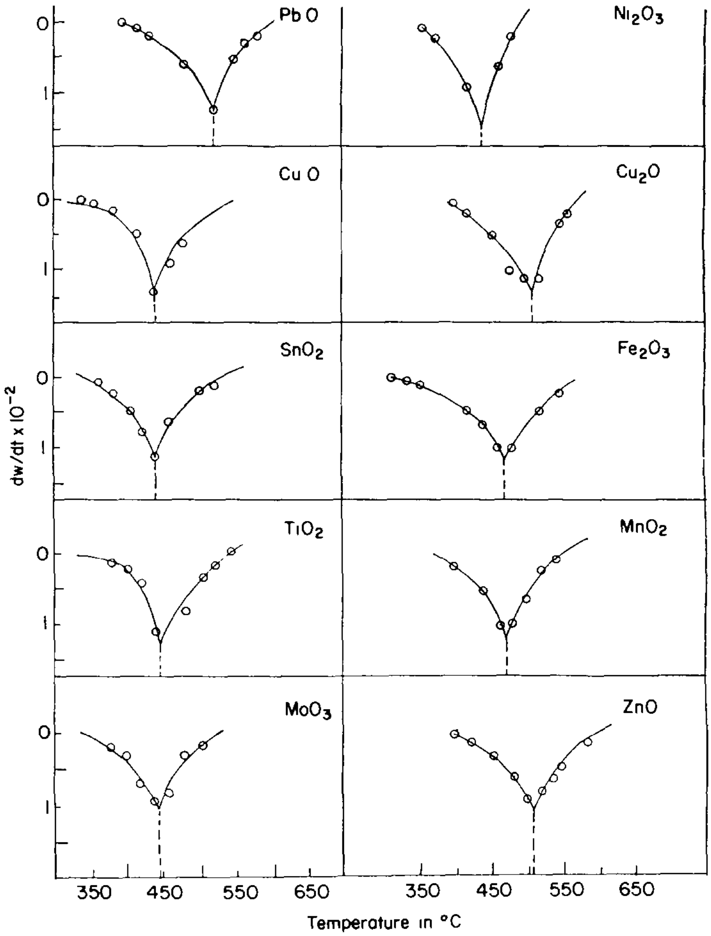

Fig. 2. DTG curve for nylon-6 mixed with different oxides and heated in air.

data could be used to calculate the kinetic parameters and then to study the compensation effect in order to understand the underlying mechanism of the thermal oxidative degradation.

EVALUATION OF THE KINETIC PARAMETERS

It is generally accepted that thermogravimetric techniques measure not absolute but relative rate constants; thus, from TG data, relative or apparent kinetic rate constants, activation energies ΔE_a and the apparent pre-exponential factor A of the thermal oxidative degradation were estimated. The thermal oxidative degradation of nylon-6 involves a complex series of reaction which may involve consecutive or even parallel

TABLE 2

Kinetic parameters and the temperature at maximum rate of decomposition

Additive	A/min^{-1}	ΔE_a/kJ mol^{-1} (±7 kJ mol^{-1})	Temperature at maximum rate of decomposition T_m/°C
None	5.01×10^{10}	178	480
CuO	1.58×10^{8}	146	420
V_2O_5	1.0×10^{5}	86	420
SnO_2	1.99×10^{6}	110	440
Cu_2O	3.16×10^{7}	127	440
Ni_2O_3	3.16×10^{7}	126	440
M_0O_3	5.01×10^{3}	76	445
TiO_2	3.98×10^{7}	130	445
CeO_2	1.26×10^{7}	124	460
ZrO_2	1.58×10^{7}	124	470
Fe_2O_3	1.0×10^{7}	172	470
MnO_2	2.51×10^{10}	174	470
Sb_2O_3	3.16×10^{6}	122	500
Cr_2O_3	3.96×10^{8}	157	505
ZnO	6.31×10^{7}	147	505
PbO	3.96×10^{7}	148	520

and branched chain reactions. Sagar [4] and Sebenda et al. [5] have shown that, in the presence of oxygen, polyamides undergo thermal oxidation through the formation of hydroperoxide, which is autocatalytic. However, the rate in the initial stages is proportional to the concentration of the polyamide and these hydroperoxides are thermally decomposed via non-radical routes. The present studies were carried out in limited air. The apparent kinetic parameters of the thermal oxidative degradation were estimated from the TG data using the Sharp–Wentworth Method [6]. It is assumed that the thermal oxidative degradation of nylon-6 is first order; the Sharp–Wentworth equation can be written as

$$\log \frac{(\mathrm{d}w/\mathrm{d}T)}{1-w} = \log n(A/\beta) - \Delta E_a/2.303RT \tag{1}$$

where w is the fractional mass loss and $\mathrm{d}w/\mathrm{d}T$ gives the rate of mass loss as a function of temperature, A is the pre-exponential factor, β is the rate of heating and ΔE_a is the activation energy. A plot of the left hand side of eqn. (1) as a function of the reciprocal of temperature ($1/T$) should give a straight line, from whose slope and intercept the apparent kinetic parameters can be obtained.

A typical Sharp–Wentworth plot (left hand side of eqn. (1) vs. $1/T$) for

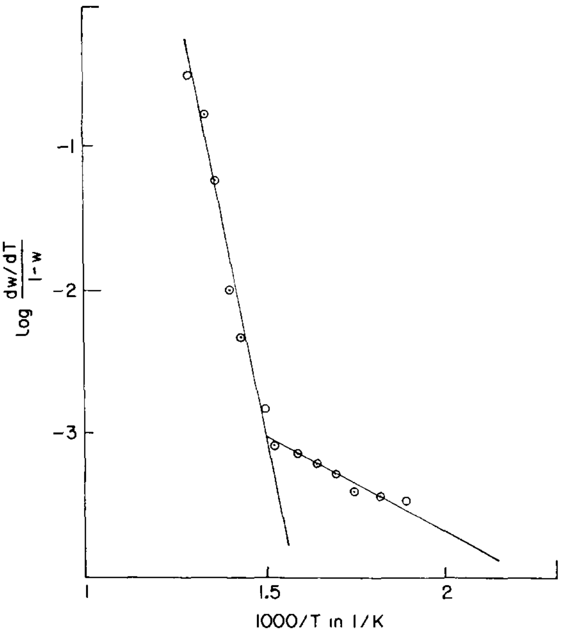

Fig. 3. Activation energy from Sharp–Wentworth method.

nylon-6 and metal oxide mixture is shown in Fig. 3, and the apparent activation energies and pre-exponential factors for oxidative degradation of nylon-6 in the presence of different metal oxides are given in Table 2.

The kinetic compensation effect

The calculation of kinetic parameters demonstrates the temperature dependence of the rate of thermal oxidative degradation of nylon-6, which is represented by the Arrhenius equation, and shows that these parameters vary with experimental conditions. That is, the value of the kinetic parameters is different for mixtures of nylon-6 with different metal oxides. However, it is most unusual to find two closely similar heterogeneous reactions both of which obey the Arrhenius rate law but with different activation energies that have the same pre-exponential factor A. In order to correlate the value of the pre-exponential factor A and the activation energy ΔE_a, a relationship between $\ln A$ and ΔE_a is established which shows that two reactions must proceed at the same rate at some temperature called the isokinetic temperature T_{iso} within the range of experimental temperature. If similar behaviour is also shown by a larger group of heterogeneous reactions, a plot of $\ln A$ against ΔE_a often yields a good fit to a straight line of positive slope represented as

$$\ln A = \ln k_{iso} + \Delta E_a/RT_{iso} \qquad (2)$$

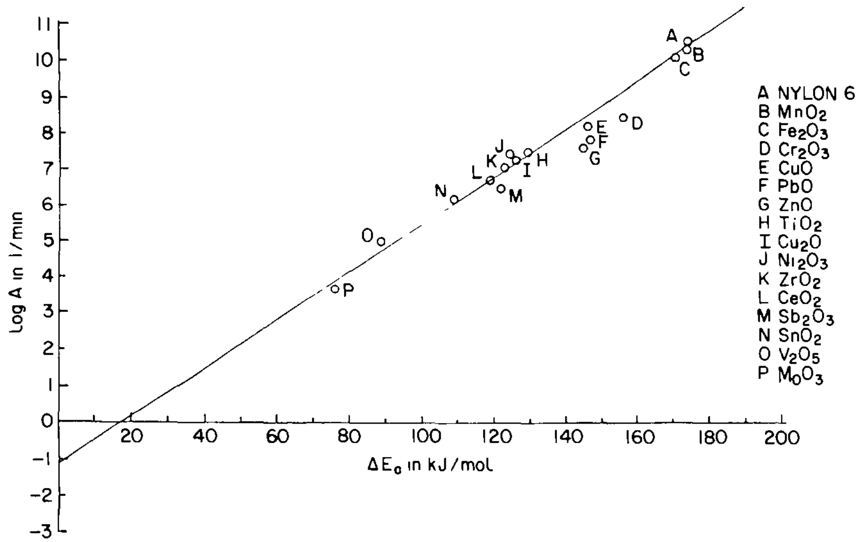

Fig. 4. Correlation between log A and ΔE_a.

where T_{iso} and k_{iso} are the average isokinetic temperature and the average rate constant at $T = T_{iso}$. This is usually referred to as the "compensation effect" (c.e.) or "isokinetic effect" [7].

Thus a relationship was sought between log A and ΔE_a from the values listed in Table 2, and a plot of log A versus ΔE_a is given in Fig. 4. This shows that a linear relationship exists between log A and ΔE_a and that the thermal oxidative degradation of nylon-6 in the presence of metal oxide has a reaction rate compensation effect which is normally associated with the variation of kinetic parameters of a heterogeneous reaction on different solids.

Fitting the data in Fig. 4 gave the following expression with a correlation coefficient of 0.98

$$\log A = 0.062(\pm 0.016)\Delta E_a - 1.15(\pm 2.45) \qquad (3)$$

The figures in parentheses represent error limits of 95% confidence.

This means that there is a compensation between activation energy and pre-exponential factor in the thermal oxidative degradation of nylon-6 in the presence of metal oxides. The isokinetic temperature T_{iso} at which the reaction rates are equal is 569°C and the isokinetic reaction rate constant, $\log k_{iso} = -1.15\ \text{min}^{-1}$.

Evidence for such compensating behaviour is reported in numerous studies [8–12] and several theories predict such linear compensation behaviour [8,13–16]. These theories suggest that its occurrence is probably due to an enthalpy–entropy relationship; tunnelling effect; relationship between the entropy of transitions and the change in energy levels in the transiton state; simultaneous occurrence of reactions on surface centres involving different activation energies, and due to the existence of interrelated kinetic behaviour within a group of rate processes. The isokinetic temperature has been suggested as a temperature at which relative reaction rates within groups of related reactions undergo inversion, or as representing the temperature at which the rate constants of all reactions of the series have the same value [8, 17].

However, the existence of a compensation effect in heterogeneous reactions has been suggested, and numerous occurrences of compensation behaviour have been reported in the literature. Agrawal [14] has suggested an alternative and more reliable method of detecting compensation behaviour by an Arrhenius plot of log k vs. the reciprocal temperature ($1/T$). The occurrence of a true compensation effect is displayed when the Arrhenius plots show a point of concurrence. If Arrhenius plots display no such concurrence at a single point, then the reaction system exhibits no compensation effect. An Arrhenius plot of $\log k$ vs. $1/T$ for the thermal degradation of nylon-6 in the presence of metal oxides, from the non-isothermal TG data, is shown in Fig. 5. The Arrhenius plot clearly indicates a concurrence chiefly for transition metal oxides such as those of V(V), Zr(IV), Ti(IV), Fe(III), Mn(IV), Ni(III), Ce(IV), Cu_2(II) and Sn(IV). Oxides such as those of Cu(II), Pb(II), Sb(III), Mo(IV), Cr(III) and Zn(II) do not indicate concurrence at the same point. The isokinetic temperature and isokinetic rate constant from Fig. 5 are 560°C and

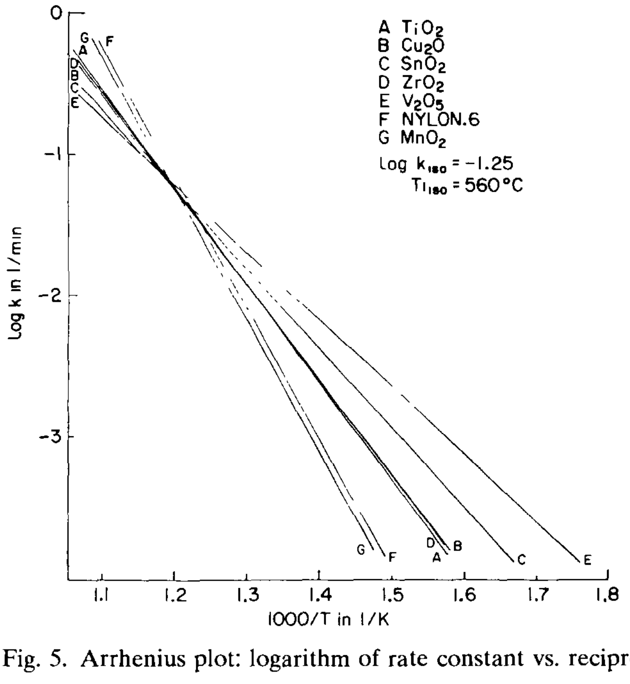

Fig. 5. Arrhenius plot: logarithm of rate constant vs. reciprocal of absolute temperature.

$-1.2\,\text{min}^{-1}$ respectively. These compare well with the values determined from the $\log A$ vs. ΔE_a plot in Fig. 4. Further, in Fig. 4 it can be noted that data for metal oxides which do not exhibit concurrence do not lie exactly on the same line. At isokinetic temperature T_{iso} the thermal degradation of nylon-6 in presence of transition metal oxides proceeds at the same rate. Above T_{iso}, the faster reactions have a higher activation enegy and below T_{iso}, faster reactions have a lower activation energy.

Ranganathan et al. [18] investigated the usefulness of the c.e. in evaluating catalysts, and reported that catalysts having different bulk properties had different $\log k_{\text{iso}}$ values, whereas those with similar bulk property but different surface properties exhibit the same $\log k_{\text{iso}}$. Also, $\log k_{\text{iso}}$ was reported to be least susceptible to changes in physical structure or method of preparation of the catalyst. They therefore suggested that $\log k_{\text{iso}}$ can be used to correlate bulk properties but not surface properties. In the present studies $\log k_{\text{iso}}$ and T_{iso} were the same for each of the transition metal oxides and could be considered as unique for the decomposition reaction.

As discussed earlier, the activity of metallic oxides to catalyse the oxidative degradation of nylon-6 was observed mainly for metal oxides in their higher oxidation state, and was largely independent of seimconductor properties (n-type or p-type). It is therefore suggested that metal oxides catalyse the thermal degradation of nylon-6 as a redox or electron transfer reaction of the type.

$$\text{ROOH} + e \rightarrow \text{RO}^{\bullet} + \text{OH}^- \qquad \text{(I)}$$

$$\text{ROOH} + p \rightarrow \text{ROO}^{\bullet} + \text{H}^+ \qquad \text{(II)}$$

where ROOH is the hydroperoxide of nylon-6 which is formed by the reaction between nylon-6 and O_2 at elevated temperature and acts as a weak link on the polymer backbone [4,19–21]. The macroradicals such as $\text{RO}^{\bullet}$ are chain initiators in the thermal oxidative deegradation of nylon-6 [20, 21].

Another property of the metal oxides which can be correlated with the observed rates is the forbidden energy band gap. Thus, Fig. 6 shows that there is a general correlation between the activation energy and the forbidden energy band gap. The good correlation between ΔE_a and the energy band gap strengthens the suggestion that nylon-6 undergoes thermal oxidative degradation via a redox mechanism and that the true compensation effect may be considered as the basis for the study of themal oxidative degradation of polymers.

The differences in the rates of thermal oxidative degradation of nylon-6 in the presence of metal oxides can be explained by the mechanism which is responsible for the c.e. in this type of reaction. Cremer [7] has reported that the cause of electron transfer reactions in metal ions with variable

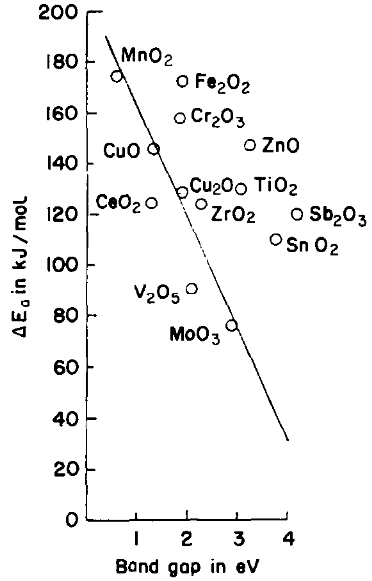

Fig. 6. Activation energy vs. band energy gap.

oxidation state is the "tunnel effect". Thus, if in a reaction an electron rather than a hole tunnels (as in step (II), above), the transition probability for an electron to tunnel is much more than for a hole owing to its small mass. Therefore, the "tunnel effect" may account for the observed rates of the thermal oxidative degradation of nylon-6 in which electron transiton can be considered as an essential step (step (I)).

If a "tunnel effect" takes place, the transition coefficient τ_e appears on the right hand side of the Eyring equation for the rate constant in activated complex theory, which is given as

$$\tau_e = \exp\left\{\left(\frac{-8\pi r}{3h}\right)[2m(V - W)]^{1/2}\right\} \tag{4}$$

Here V is the height of the energy barrier, W is the excess energy of the tunnelling electron, m is its mass and r is the width of the barrier. The formula shows that the higher the excess energy W ($\approx \Delta E_a$) the larger the probability of tunnelling and the larger also the pre-exponential factor A. Therefore, $\log A$ vs. ΔE_a will display a compensation effect.

CONCLUSIONS

A true compensation effect, which accounts for the linearity of $\log A$ with ΔE_a and concurrence to a single point of $\log k$ vs. $1/T$, is identified for non-isothermal oxidative degradation of nylon-6 in the presence of metal oxides, which may be caused by the tunnelling of an electron. It follows from this that the correct degradation mechanism is closely related to the type and the energy band gap of metal oxide semiconductors. This suggests that the process is a redox or electron transfer reaction in which electron tunnelling takes place.

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