Notes to the Editor

Estimation of energies of activation for thermal oxidation of polyolefins*

S. M. Gabbay† and S. S. Stivala
Department of Chemistry and Chemical Engineering, Stevens Institute of Technology, Hoboken, New Jersey 07030, USA
(Received 26 October 1977; revised 14 February 1978)

INTRODUCTION

Stivala and Reich have previously presented a scheme for polyolefin autoxidation[1,2] which was applied to isotactic polypropylene (IPP)[3], atactic polypropylene (APP)[4], isotactic poly(1-butene) (IPB)[5], atactic poly(1-butene) (APB)[6], isotactic poly(1-pentene) (IPP-1)[7], isotactic poly(4-methyl-1-pentene) (IPMP)[8], and atactic poly(4-methyl-1-pentene) (APMP)[8], in the bulk phase in the absence of additives. The thermal oxidation kinetics of films of these polyolefins were studied, using infra-red spectroscopy as a function of temperature and oxygen to nitrogen ratios, by observing rates of carbonyl formation in the non-volatile products. Mathematical expressions derived from the general kinetic scheme satisfactorily explained the experimental results obtained and composite energies of activation were estimated for various steps in the scheme.

The purpose of this paper is to report on the estimation of single energies of activation for the initiation and peroxide decomposition stages in the scheme for the thermal oxidation of the polyolefins reported from this laboratory[1-9].

THEORY

For convenience, the general kinetic scheme for polyolefin autoxidation previously reported[1,2] is given in equations (1)–(9):

$$\mathrm{RH + O_2} \xrightarrow{k_1, \phi_i} \mathrm{R\cdot + HO_2^{\cdot}} \qquad (1)$$

$$\mathrm{R\cdot + O_2} \xrightarrow{k_2} \mathrm{RO_2^{\cdot}} \qquad (2)$$

$$\mathrm{RO_2^{\cdot} + RH} \xrightarrow{k_3} \mathrm{RO_2R + H\cdot} \text{ (one R may be H)} \qquad (3)$$

$$\mathrm{RO_2^{\cdot} + RH} \xrightarrow{k_4} \text{Inactive products} \qquad (4)$$

$$\mathrm{RO_2R} \xrightarrow{k_5} \mathrm{2RO\cdot} \qquad (5)$$

$$\mathrm{RO_2R} \xrightarrow{k_6} \text{Non-volatile carbonyl products} \qquad (6)$$

$$\mathrm{RO\cdot} \xrightarrow{k_7} \mathrm{R\cdot'} + \text{volatile products} \qquad (7)$$

$$\mathrm{R\cdot' + RH} \xrightarrow{k_8} \mathrm{R\cdot + R'H} \qquad (8)$$

$$\mathrm{R\cdot' + O_2} \xrightarrow{k_9} \text{Less reactive products} \qquad (9)$$

where RH = polyolefin chain and ϕ_i = rate of initiation.

The pertinent expressions which were derived are summarized in equations (10)–(14)

$$\rho_m = \frac{K_1[\mathrm{O_2}]}{1 - K_2/(K_3 + [\mathrm{O_2}])} \qquad (10)$$

where ρ_m is the maximum rate of formation of non-volatile carbonyl products at a certain temperature.

$$K_1 = \frac{Ck_1k_3k_6[\mathrm{RH}]}{(k_3 + k_4)(k_5 + k_6)} \qquad (10a)$$

and $C = [1 - \exp(-At_m)] \approx$ constant since at ρ_m the product At_m (where t_m is the time to reach ρ_m) is approximately constant under the experimental conditions.

$$K_2 = \frac{2k_3k_5k_8[\mathrm{RH}]}{k_9(k_3 + k_4)(k_5 + k_6)} \qquad (10b)$$

$$K_3 = \frac{k_8}{k_9}[\mathrm{RH}] \qquad (10c)$$

$$\frac{\rho_m A}{[\mathrm{O_2}]} = \frac{Ck_1k_3k_6[\mathrm{RH}]}{(k_3 + k_4)} \qquad (11)$$

$$k_5 = \frac{(k_3 + k_4)k'K_2}{2k_3K_3} \qquad (12)$$

$$A' = 1 - \frac{K_2}{K_3 + [\mathrm{O_2}]} \qquad (13)$$

where

$$A' = \frac{A}{k'} = \frac{A}{k_5 + k_6} \qquad (13a)$$

and

$$-\ln(\rho_m - \rho)/\rho_m = At \qquad (14)$$

when $\rho \ll \rho_m$

Using equations (10a)–(12), the slopes of the Arrhenius plots of $\ln K_3$, $\ln K_2/K_1K_3$, $-\ln(\rho_mA/[\mathrm{O_2}])$, and $-\ln k'K_2/K_3$ *versus* $1/T$ afforded the activation energies $(E_8 - E_9)$, $(E_1 + E_6 - E_5)$, $(E_1 + E_6)$ and E_5, respectively, where the subscripts correspond to the steps in the kinetic scheme.

RESULTS AND DISCUSSION

In light of recent work on the thermal oxidation of IPP-1, IPMP and APMP[7-9] it can be shown that energies of activation for steps (1) and (6) in the kinetic scheme can be estimated as indicated below.

From the Arrhenius plot of $-\ln k'K_2/K_3$ *versus* $1/T$ which afforded E_5, the intercept yields $\ln Z_5$, where Z_5 is the frequency factor (pre-exponential factor) for step (5). The rate constant k_5 is then calculated at different temperatures. From the derived mathematical expressions, k' represents the sum of $k_5 + k_6$ (equation 13a) which is calculated from the ratio of A/A' at different temperatures. Therefore, k_6 can be obtained at different temperatures and an Arrhenius plot of $\ln k_6$ *versus* $1/T$ will give E_6. E_1 is then calculated from the sum of $E_1 + E_6$.

Values of E_1, E_5 and E_6, calculated for IPP, IPB, APB, IPP-1, APMP, and

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* Presented at the 15th Prague IUPAC Microsymposium 'Degradation and Stabilization of Polyolefins', July 1975.

† Present address: PPG, Pittsburg, Pennsylvania, USA.

0032–3861/78/1907–0850$01.00

Table 1 Single activation energies for the thermal oxidation of various polyolefins

Activation energy (kcal/mol)	IPP	APP	IPB	APB	IPP-1	IPMP (below 150°C)	IPMP (above 150°C)	APMP
E_1	21	18	16	18	21	10	10	13
E_5	29	29	25	22	26	17	19	27
E_6	24	30	22	19	25	23	18	30

IPMP (above and below 150°C) are listed in *Table 1*. In the case of IPP, APP, IPB, and APB, the values of the various kinetic parameters (i.e. K_1, K_2, K_3, ρ_m, A, k') used to estimate E_1 and E_6 were refined and recalculated as described elsewhere[9]. From *Table 1*, different values of E_1 may be noted which may be attributed to the different nature and identity of the polyolefin chain in the initiation step. It is possible that the values of E_1 may be somewhat low for step (1). In the case of low hydrocarbons Russel[10] studied the oxidation of indene and found that the kinetics of the reaction were consistent with the initiation process as in step (1). The activation energy for the reaction was estimated as 25 kcal/mol from the R–H bond energy and the dissociation energy of H–O_2. Further, by assuming a steric factor of 10^{-3} and a collision number of 10^{11}, $k_1 = 10^8\exp(-25\,000/RT)$. The calculated value of k_1 for the indene oxidation at 50°C was found to be in good agreement with the experimental value at 50°C. In the case of the polyolefins, relative to values of E_1 (of *Table 1*), it would be noteworthy to consider or take into account the influence of metal catalyst[1]. Polyolefins may contain trace metals as residuals from the Ziegler–Natta catalysis of the olefins. For example, the lower value of E_5 for IPB compared with APB was attributed by Stivala, Yo and Reich[5] to the presence of various trace metals in the isotactic poly(butene-1) sample detected from its ash by spectroscopy.

Values of E_6 activation energy for the decomposition step of peroxides yielding non-volatile carbonyl products for APP was reported as 27 kcal/mol by Nieman[11] and a value of 21 kcal/mol for IPMP was reported recently by Zitomer and DiEdwardo[12].

REFERENCES

1 Reich, L. and Stivala, S. S. Autoxidation of Hydrocarbons and Polyolefins', Marcel Dekker, New York, 1969

2 Reich, L. and Stivala, S. S. 'Elements of Polymer Degradation', McGraw-Hill, New York, 1971

3 Stivala, S. S., Reich, L. and Kelleher, P. G. *Makromol. Chem* 1963, 59, 28

4 Jadrnicek, B. R., Stivala, S. S. and Reich, L. *J. Appl. Polym. Sci.* 1970, **14**, 2537

5 Stivala, S. S., Yo, G. and Reich, L. *J. Appl. Polym. Sci.* 1969, **13**, 1289

6 Stivala S. S., Kaplan, E. B. and Reich, L. *J. Appl. Polym. Sci.* 1965, 9, 3557

7 Gabbay, S. M., Stivala, S. S. and Reich, L. *Polymer* 1975, **16**, 749

8 Gabbay, S. M. and Stivala, S. S. *Polymer* 1976, **17**, 137

9 Gabbay, S. M., *PhD Thesis* Stevens Institute of Technology, Hoboken, New Jersey, USA (1975)

10 Russel, G. A. *J. Am. Chem. Soc.* 1956, 78, 1047

11 Neiman, M. B. 'Aging and Stabilization of Polymers', Consultant Bureau, New York, (1975)

12 Zitomer, F. and DiEdwardo, A. H. *J. Macromol. Sci. (A)* 1974, 8, 119

Non-linear electric behaviour of polymeric materials interpreted through free volume changes

F. P. La Mantia and D. Acierno

Istituto di Ingegneria Chimica, Università di Palermo, Palermo, Italy

(Received 3 January 1978; revised 7 February 1978)

INTRODUCTION

The electrical behaviour of polymeric materials has received much attention because some of the properties peculiar to polymers may find useful applications. The change of resistivity with temperature[1], the relationship between the applied electrical field and the resulting current[2,3] and the dielectric rigidity[4] may be considered typical examples of such studies.

The occurrence of non-linear electric phenomena in these materials is generally attributed both to the temperature rise due to the circulating current (especially relevant in the case of an alternating current) and to the direct influence of the applied field. If, as an example, the stress aging phenomenon is considered, i.e. the degradation in time of the electrical characteristics when a field is applied, the process rate, v, is assumed to be[5]:

$$v = aT^w \exp(-b/kT) \times \exp\{f(V)[c + (d/kT)]\} \qquad (1)$$

where a, b, c, d and w are material constants, k is Boltzmann's constant, T is the absolute temperature and $f(V)$ is a function of the applied voltage. In equation (1) the effect of temperature is taken into account through an Arrhenius-type dependence and that of the electrical field through the Eyring model.

In this work a possible interpretation of non-linear effects is advanced in terms of 'free volume'. Use will be made of concepts analogous to those already applied in considering nonlinearities in the rheological behaviour of polymeric systems.

ANALOGY BETWEEN ELECTRICAL AND MECHANICAL BEHAVIOUR

Viscosity and resistivity depend upon temperature in a similar way. This dependence is often written as:

$$\eta = A \exp\left(\frac{E_a}{RT}\right) \qquad (2a)$$

$$\rho = B \exp\left(\frac{E_a}{RT}\right) \qquad (2b)$$

where η and ρ are viscosity and resistivity, respectively; E_a is activation energy and A and B are frequency factors.

0032–3861/78/1907–0851$01.00