HEAT TRANSFER EFFECTS DURING TEFLON DEGRADATION BY TGA

LEO REICH

Polymer Research Branch, Picatinny Arsenal, Dover, N. J. 07801 (U.S.A.)

AND S. S. STIVALA

Department of Chemistry and Chemical Engineering, Stevens Institute of Technology, Hoboken, N. J. 07030 (U.S.A.).

(Received July 21st, 1969)

ABSTRACT

Heat transfer effects during Teflon degradation by TGA were studied. Cylindrical samples were embedded in a thermal insulator so that only one of the faces was exposed. These insulated samples were then subjected to thermal degradation by means of TGA in a helium atmosphere. Above a Teflon-sample thickness of about 50–65 mils, a first-order plot afforded low values of activation energy (E) of 48–53 kcal·mole^{-1}. However, at higher conversions, values of $E = 85$–88 kcal·mole^{-1} obtained. When heat transfer effects were taken into account by the use of an appropriate equation, values of $E = 86$–88 kcal·mole^{-1} were obtained at the lower conversions. An insulated Teflon sample whose thickness was 27 mils afforded a value of $E \approx 77$ kcal·mole^{-1}, based on a first-order plot, over a wide conversion range.

INTRODUCTION

It has been observed[1] that when values of activation energy (E) for Teflon degradation were determined by means of dynamic thermogravimetric analysis (TGA)[2-10], they were generally lower than those obtained from isothermal experiments[11-13]. Thus, values of E in the former case ranged from 66 to 77 kcal·mole^{-1} whereas values of E in the latter case varied from 80.5 to 83 kcal·mole^{-1}. (However, values of reaction order (n) were consistently close to unity in both cases.) The preceding suggested that there were factors affecting values of E during TGA experiments which were less operative in the case of isothermal experiments. One such factor may be heat transfer effects which would be expected to occur preferably during TGA experiments due to the dynamic nature of such experiments. (The use of small, finely powdered samples or very thin-filmed samples usually employed in TGA should minimize such effects.) It was thus decided to investigate the effects of heat transfer upon values of E during Teflon degradation by TGA.

EXPERIMENTAL

Commercially available Teflon (DuPont) cylindrical rods were lathed and cut into various cylindrical sample sizes. These samples were then embedded in a Transite

thermal insulator so that only one face of the cylindrical sample was exposed. Various average sample sizes (diameter and thickness in inches) and their designation code are listed in the following: $3/16 \times 1/16$ (1T), $1/8 \times 3/32$ (3T), and $3/16 \times 1/37$ (5T).

The above samples were then placed in a 950 DuPont Thermogravimetric Analyzer (the Teflon sample weights varied from 25 to 66 mg while the sample weights including the insulator varied from 60 to 120 mg). The TGA apparatus was programmed for a heating rate of 2°C per min and an atmosphere of helium (approx. 40 cm^3 per min) was maintained around the sample during each run. A blank run indicated that the rate of weight loss of Transite was very small above 500°C (at which temperature incipient degradation of Teflon becomes important).

THEORY

The one dimensional heat conduction equation without chemical reaction or radiative cooling may be written for a solid as

$$C\rho \frac{\partial T}{\partial t} = K \frac{\partial^2 T}{\partial x^2} \tag{1}$$

where, T = temperature in a solid at position x at time t; K = thermal conductivity; C = specific heat; ρ = density. (Values of K, C, and ρ are assumed to be constant during a TGA run.) When chemical reaction is included, Eqn. 1 becomes

$$C\rho \frac{\partial T}{\partial t} = K \frac{\partial^2 T}{\partial x^2} + q \tag{2}$$

where, q = amount of heat absorbed by the chemical reaction in a unit volume per unit time. Assuming that the Arrhenius law is applicable and that Teflon degradation involves a first-order reaction, we may write

$$q = -QA\rho \, e^{-E/RT} \tag{3}$$

where, Q = thermal factor, A = frequency factor, and the minus sign indicates that heat is absorbed. Combining Eqns. 2 and 3 gives

$$C\rho \frac{\partial T}{\partial t} = K \frac{\partial^2 T}{\partial x^2} - QA\rho \, e^{-E/RT} \tag{4}$$

It is now assumed that

$$\frac{\partial T}{\partial t} \ll \frac{QA \, e^{-E/RT}}{C} \tag{4'}$$

That this is justified may be seen from various values reported[13]. Thus, if we assume $E = 83$ kcal·mole^{-1}, $Q = 400$ cal/g (enthalpy of depropagation), $A = 3 \times 10^{19}$ sec^{-1}, $C = 15 + 0.034T$ cal·mole^{-1}·degree^{-1} (strictly applicable only up to 120°C), and

$T = 800\,^\circ K$, and if we assume that $\partial T/\partial t$ may be well approximated by $0.033\,^\circ C \cdot sec^{-1}$ (heating rate), then $0.03 \ll 1$ and Eqn. 4' is justified. Eqn. 4 now becomes

$$\frac{d^2 T}{dx^2} = \frac{Q}{K} A\rho\, e^{-E/RT} \tag{5}$$

Let us assume the following boundary conditions for the insulated Teflon samples, $x = 0$, $T = T_0$; $x = l$, $\dfrac{dT}{dx} \ll \dfrac{dT}{dx}\bigg|_{x=0}$, $T = T_l$, where l = thickness of sample which is involved in heat transfer effects. Eqn. 5 may be readily integrated to give

$$\frac{dT}{dx}\bigg|_{x=0} = \left(\frac{2\,Q A\rho R}{KE}\right)^{1/2} T_0\, e^{-E/2\,RT_0} \tag{6}$$

provided that $T_l \ll T_0$ and $2RT/E \ll 1$ (lit.[14,15]). It can also be shown that

$$\rho_t \equiv -\frac{dW}{dt} = \frac{KS}{Q}\frac{dT}{dx}\bigg|_{x=0} \tag{7}$$

where, S = cross-sectional area and W is the weight of Teflon remaining during degradation. By combining Eqns. 6 and 7, there is finally obtained

$$\frac{\rho_t}{T_0} = S\left(\frac{2KA\rho R}{QE}\right)^{1/2} e^{-E/2\,RT_0} \tag{8}$$

Several remarks in regard to Eqn. 8 are apropos at this point. Since the thermal degradation of Teflon by TGA occurs over a relatively small temperature range and since these temperatures are high (about $800\,^\circ K$), $\rho_t/T_0 \approx const. \times \rho_t$. Thus, Eqn. 8 resembles a zero-order reaction. It has been previously indicated[14,15] that at relatively low conversions, the degree of conversion as a function of temperature is independent of reaction order. In view of the preceding and Eqn. 8, when a thermal barrier is controlling during the TGA degradation of Teflon, a first-order plot should afford a value of E which is approximately one-half the value that would be obtained in the absence of strong heat transfer effects. For the first-order degradation of Teflon[1],

$$\log(\rho_T/W) = -E/4.6\,T + \log[A/(RH)] \tag{9}$$

where $\rho_T = \rho_t/RH \equiv -dW/dT$ and (RH) = heating rate.

When $\log(\rho_T/W)$ is plotted against $1/T$ (cf. Eqn. 9), the value of E should be approximately one-half that value of E obtained from a plot of $\log(\rho_T/T_0)$ vs. $1/T$ (cf. Eqn. 8), when heat transfer effects are important. It may also be remarked here that derived data was obtained for the Teflon degradation only up to conversions of about 50%. Beyond this conversion, the slopes of the primary thermograms became too steep to utilize satisfactorily.

RESULTS AND DISCUSSION

In Fig. 1 are depicted plots of Eqns. 8 and 9 for runs 1T and 3T. From this figure, it can be seen that for run 1T, a first-order plot afforded a value of $E \approx 48$ kcal/mole up to about 15% conversion. However, after about 20% conversion, the value of E changed drastically and possessed a value of about 88 kcal/mole. Similarly, for run 3T, up to a conversion of about 21%, the value of $E \approx 53$ kcal·mole^{-1}
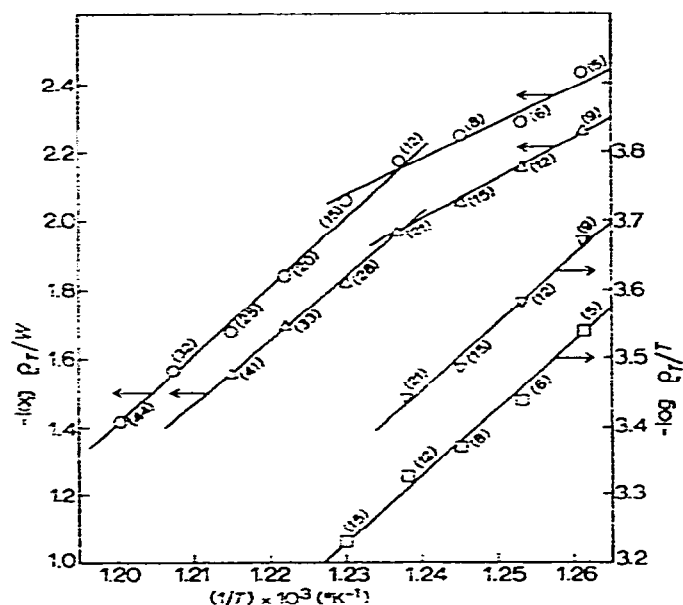

Fig. 1. Plots of $-\log \varrho_T/W$ and $-\log \varrho_T/T$ against $1/T$. O and □, run 1T; △ and ▽, run 3T. (Values in parentheses on plots denote percentage conversion.)

whereas after about 28% conversion the value of $E \approx 85$ kcal·mole^{-1}. When Eqn. 8 was employed for the data of runs 1T and 3T at low conversions (where $E \approx 48$ and 53 kcal·mole^{-1}), linear relationships were obtained which afforded values of $E \approx 88$ kcal·mole^{-1} (run 1T) and $E \approx 86$ kcal·mole^{-1} (run 3T). Thus, it would appear that when heat transfer effects are taken into account, values of E can be obtained which are of the correct order of magnitude. Otherwise, low values of E are obtained.

From Fig. 1 and sample sizes, it was observed that heat transfer effects diminish considerably or become negligible at cylindrical sample thicknesses below 50–65 mils. To test this observation, a cylindrical Teflon thickness of 27 mils (run 5T) was utilized in a TGA degradation. In Fig. 2 can be seen a plot of Eqn. 9 for this sample size. A fairly good linear relationship was obtained, commencing at the relatively low conversion of about 8%, which afforded a value of $E \approx 77$ kcal·mole^{-1}. In this connection, it may be noted that Siegle and co-workers[13] degraded a 60-mil Teflon film isothermally at 480°C and observed that during the early conversions, the first-order rate constant was of much smaller magnitude than at later conversions.

These workers also observed that when thin films (about 2 mils) of Teflon of low melt index were degraded isothermally at 480°C, the first-order plot assumed a sigmoid-type curve and that the value of the rate constant at higher conversions became similar to that obtained for the degradation of thin Teflon films (about 2 mils) of higher melt index, at 480°C. These effects were attributed to the diffusion barrier which resulted from sample thickness.
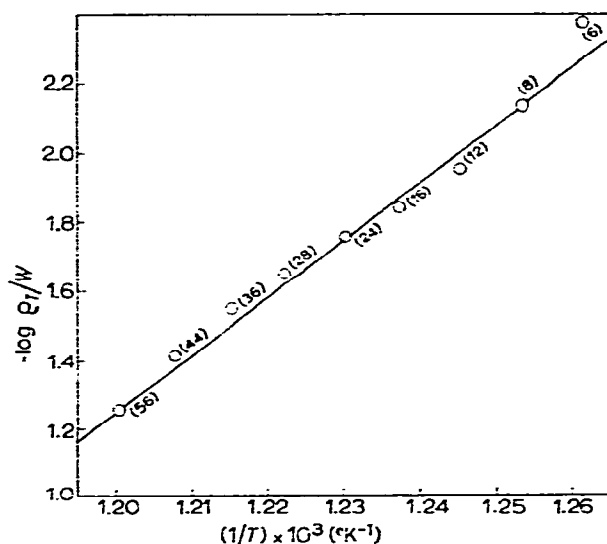

Fig. 2. Plot of $-\log \varrho_T/W$ against $1/T$ (run 5T). (Values in parentheses on plot denote percentage conversion.)

From Eqn. 8, it can be seen that when heat transfer effects are important the ratio ρ_T/T should be proportional to the surface area of the exposed cylindrical sample face. Thus, for runs 1T and 3T at low conversions, the ratio $\rho_T(3T)/\rho_T(1T)$ should be about 0.5. The observed ratio was found to be about 0.7. While this agreement is not too good, it should be remembered that Eqn. 8 is only considered to be approximate, that the surface area S may not remain constant during Teflon degradation, and that sample dimensions are not exact.

If we extend this work, it would appear that when heat transfer effects become important during TGA degradations (due to conglomeration, melting, etc.), and when linear first-order plots are constructed, lower average values of E should obtain than when heat transfer effects are absent. This may be true in the case of Teflon (cf. INTRODUCTION). In the case of isothermal degradation of Teflon, these heat transfer effects may be minimal due to better control of experimental conditions, e.g., isothermal degradation of a sample may be carried out well below the sintering point of the sample, and better temperature equilibrium may be established.

REFERENCES

i L. REICH AND D. W. LEVI, in A. PETERLIN, M. GOODMAN, S. OKAMURA, B. H. ZIMM, AND H. F. MARK (Eds.), Macromolecular Reviews, Vol. 1, Interscience, New York, 1966, pp. 173–275.

2 C. D. DOYLE, *J. Appl. Polymer Sci.*, 5 (1961) 285.

3 H. C. ANDERSON, *Makromol. Chem.*, 51 (1962) 233.

4 L. REICH, H. T. LEE, AND D. W. LEVI, *J. Polymer Sci.*, B1 (1963) 535.

5 L. REICH AND D. W. LEVI, *J. Polymer Sci.*, B2 (1964) 1109.

6 R. M. FUOSS, I. O. SALYER, AND H. S. WILSON, *J. Polymer Sci.*, A2 (1964) 3147.

7 H. C. ANDERSON, *J. Polymer Sci.*, C6 (1964) 175.

8 L. REICH, H. T. LEE, AND D. W. LEVI, *J. Appl. Polymer Sci.*, 9 (1965) 351.

9 L. REICH, *J. Polymer Sci.*, B3 (1965) 231.

10 L. REICH, *J. Appl. Polymer Sci.*, 9 (1965) 3033.

11 S. L. MADORSKY, V. E. HART, S. STRAUS, AND V. A. SEDLAK, *J. Res. Nat. Bur. Stand.*, 51 (1953) 327.

12 S. L. MADORSKY AND S. STRAUS, *J. Res. Nat. Bur. Stand. A*, 64 (1960) 513.

13 J. C. SIEGLE, L. T. MUUS, T.-P. LIN, AND H. A. LARSEN, *J. Polymer Sci.*, A2 (1964) 391.

14 A. W. COATS AND J. P. REDFERN, *J. Polymer Sci.*, B3 (1965) 917.

15 L. REICH, *Makromol. Chem.*, 105 (1967) 223.