

## NOTES

*Application of DTA Techniques to Polymer Degradation*

## Introduction

Methods have been reported for the estimation of kinetic parameters by means of DTA techniques. However, in these methods, overall activation energy ( $E$ ) and reaction order ( $n$ ) are evaluated by trial-and-error procedures,<sup>1,2</sup> or  $E$  is estimated after assuming a value of  $n$ ,<sup>3-5</sup> or  $E$  is estimated after obtaining a value of  $n$  from thermogravimetric (TGA) traces.<sup>6</sup> In order to overcome such disadvantages, methods have been proposed<sup>7</sup> whereby both  $E$  and  $n$  may be directly obtained from DTA traces. The purpose of this paper is to present another method for the simultaneous estimation of  $E$  and  $n$ . This method was first tested by applying it to the decomposition of relatively simple substances in solution and in the solid state. It was then applied to polyethylene (PE).

## Experimental

The DTA apparatus employed consisted of a Thermoanalyzer unit (Aminco). About 100 mg. of a finely powdered sample of NaHCO<sub>3</sub> (U.S.P.) were used and the reference material employed (100 mg.) was finely powdered Al<sub>2</sub>O<sub>3</sub> (Fisher Certified Reagent, and the sample and reference cells were loosely packed. For the NaHCO<sub>3</sub>, heating rates of about 3<sup>1</sup>/<sub>2</sub> and 6°C./min. were used in still air. DTA traces previously obtained<sup>2</sup> for the decomposition of benzenediazonium chloride (BDC) in aqueous solution at various heating rates were also used. In the case of PE (Bakelite), the sample consisted of 14 mg. of PE "sandwiched" between 86 mg. Al<sub>2</sub>O<sub>3</sub> and heating rates of 8.7 and 16.1°C./min. were used.

## Results and Discussion

By assuming that heat-capacity terms are negligible in comparison with other terms and that the cell constants for the sample and reference cells are about equal, it may be shown<sup>1,8</sup> that

$$-dW/dT \cong W_0(\Delta T/A_T) \quad (1)$$

and,

$$W \cong W_0(\bar{a}_T/A_T), \quad (2)$$

where  $\bar{a}_T = \int_{T_i}^{\infty} \Delta T dT - \int_{T_i}^T \Delta T dT$ ,  $A_T = \int_{T_i}^{\infty} \Delta T dT$ ,  $\Delta T$  is the height of the DTA curve and,  $W$  and  $W_0$  denote, respectively, the weight or weight fraction of active material remaining and the original weight or weight fraction of active material present.

We may also write, assuming that the Arrhenius equation is valid in pyrolyses,

$$-dW/dT = (Z/RH) \exp \{-E/RT\} W^n \quad (3)$$

where,  $Z$  = frequency factor, and  $(RH)$  = heating rate.

By employing a single DTA trace (trace 1) for the same material and for the same value of  $\Delta T$ , before the peak ( $\Delta T_1$ ) and after the peak ( $\Delta T_1'$ ), we may write from eqs. (1-3),

$$-E/R(1/T_1 - 1/T_1') = n \ln (\bar{a}_T, 1'/\bar{a}_T, 1) \quad (4)$$

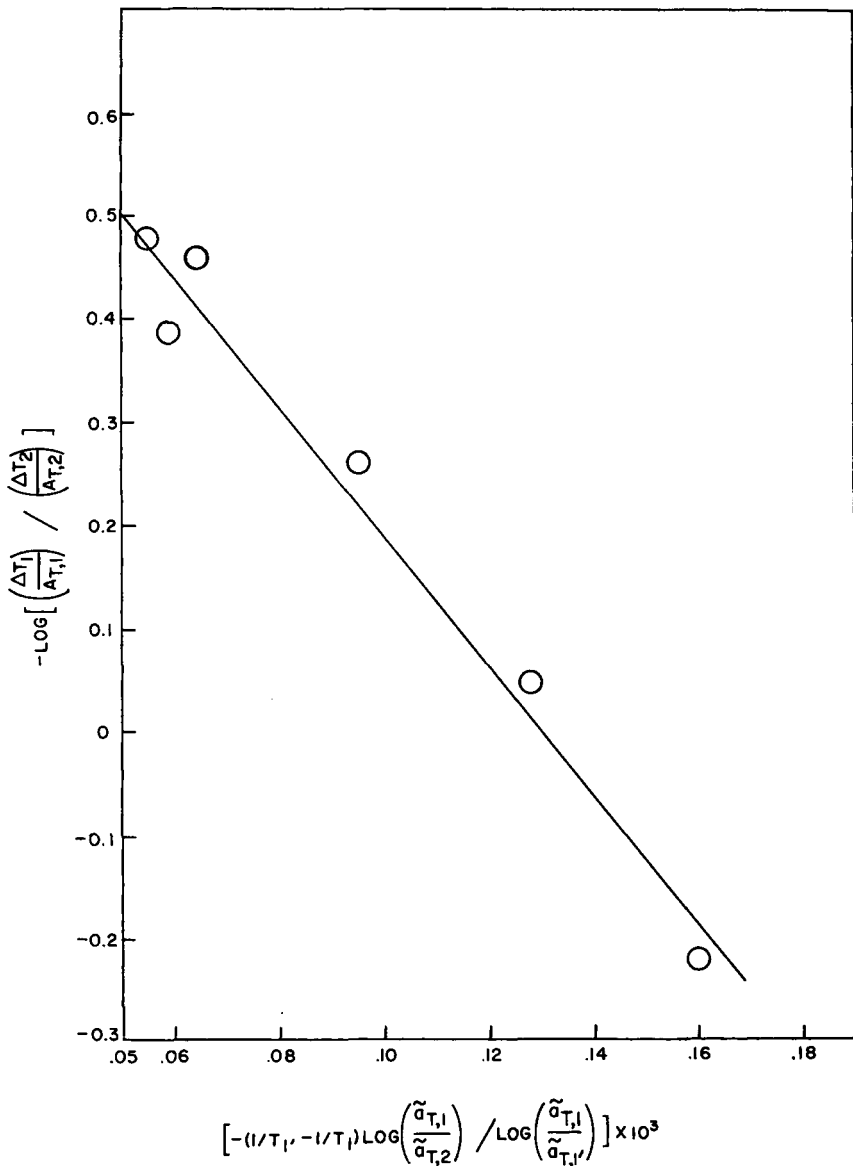


Fig. 1. Plot of eq. (6) for the decomposition of benzenediazonium chloride in aqueous solution. DTA traces at heating rates of 0.55 and 1.03°C./min. were utilized.<sup>2</sup>

Since eq. (4) involves two unknowns, another DTA trace for the same material at a different heating rate must be employed (trace 2). By utilizing an isothermal for traces 1 and 2 and employing eqs. (1-3), it may be readily shown that,

$$\ln \left[ \frac{(\Delta T_1/A_{T,1})}{(\Delta T_2/A_{T,2})} \right] = n \ln \left( \frac{\bar{a}_{T,1}}{\bar{a}_{T,2}} \right) + \ln \left( \frac{(\text{RH})_2}{(\text{RH})_1} \right) + n \ln \left( \frac{A_{T,2}}{A_{T,1}} \right) + (n-1) \ln \left( \frac{W_{0,1}}{W_{0,2}} \right) \quad (5)$$

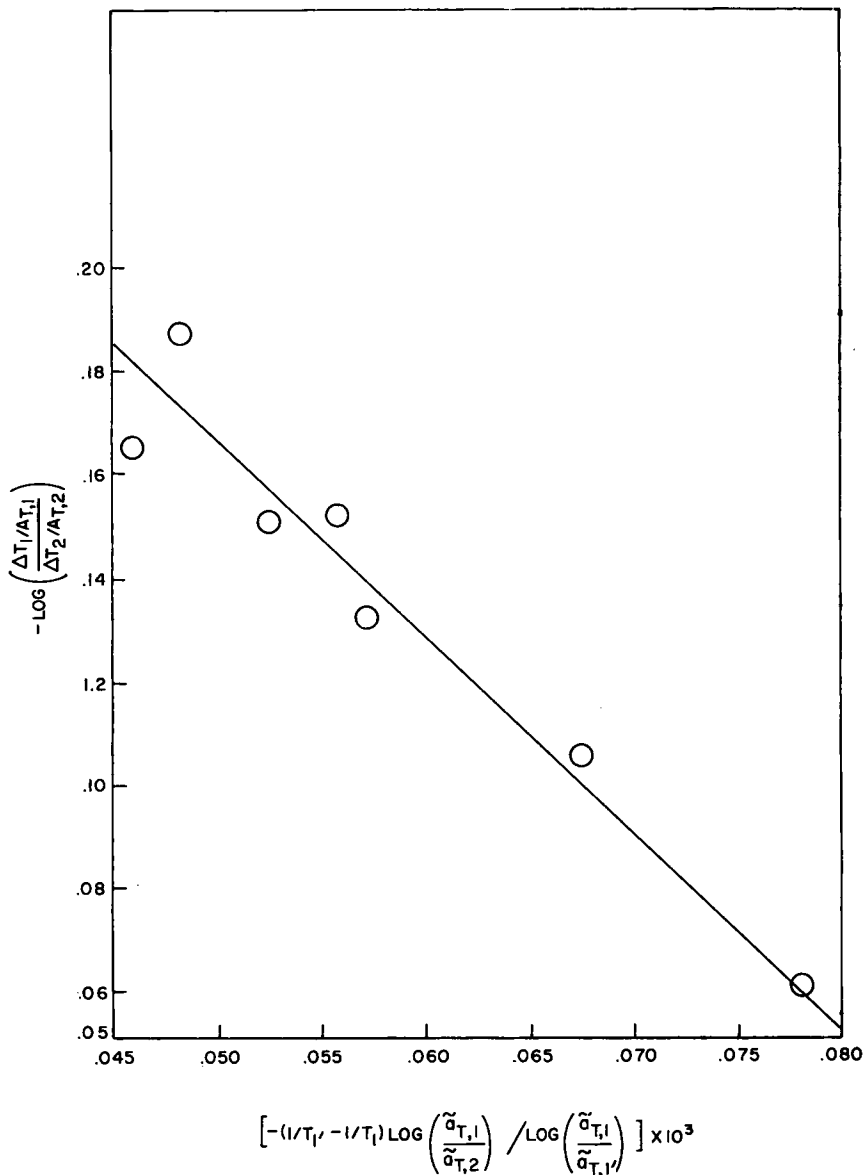


Fig. 2. Plot of eq. (6) for the decomposition of solid sodium bicarbonate. DTA traces at heating rates of 3.6<sub>5</sub> and 6.0<sub>8</sub>°C./min. were utilized.

Substituting eq. (4) into eq. (5), there is finally obtained (for the same initial weight of the material in both runs),

$$\log \left[ \frac{(\Delta T_1/A_{T,1})}{(\Delta T_2/A_{T,2})} \right] = -E/2.3R \left[ \frac{(1/T_1' - 1/T_1) \log(\tilde{\alpha}_{T,1}/\tilde{\alpha}_{T,2})}{\log(\tilde{\alpha}_{T,1}/\tilde{\alpha}_{T,1'})} \right] + \log \left( \frac{(RH)_2}{(RH)_1} \right) + n \log \left( \frac{A_{T,2}}{A_{T,1}} \right) \quad (6)$$

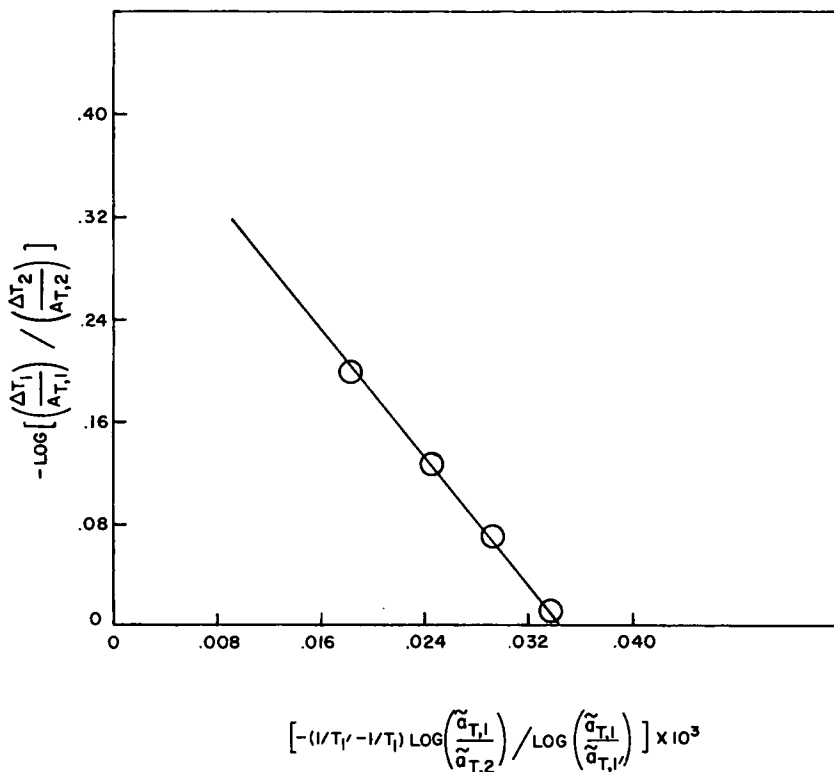


Fig. 3. Plot of eq. (6) for the decomposition of polyethylene. DTA traces at heating rates of 8.7 and 16.1°C./min. were utilized.

From a plot of the left-hand member of eq. (6) versus the first term on the right-hand side in brackets, a linear relationship should obtain whose slope will afford a value of  $E$  and whose intercept a value of  $n$ . In Figures 1, 2, and 3 are shown such plots for BDC in aqueous solution,  $\text{NaHCO}_3$ , and PE, respectively. The following values of  $E$  (kcal./mole) and  $n$  were obtained for the above materials, respectively: 29 and 1.0; 19 and 0.68; 60 and 0.7. Corresponding values reported for these materials are: 28–29<sup>18</sup> and 1.0<sup>18</sup>; 20<sup>3</sup>, 22–24<sup>9</sup> and 0.83<sup>9,2/3</sup>; 67 ± 5<sup>11</sup> and 0.82 to 1.7.<sup>11</sup> Although there appears to be a fair agreement between calculated and reported values of  $E$  and  $n$  for the materials studied by the method described in this paper, values of these parameters are sensitive to small changes in the term  $(1/T_1' - 1/T_1)$ . Thus, this term must be accurately determined in order to obtain accurate values of  $E$  and  $n$ .

#### References

1. H. J. Borchardt and F. Daniels, *J. Am. Chem. Soc.*, **79**, 41 (1957).
2. H. J. Borchardt, Ph.D. Dissertation, University of Wisconsin, Madison, 1956.
3. W. W. Wendlandt, *J. Chem. Educ.*, **38**, 571 (1961).
4. V. M. Padmanabhan, S. C. Saraiya, and A. K. Sundaram, *J. Inorg. Nucl. Chem.*, **12**, 356 (1960).
5. J. M. Haschke and W. W. Wendlandt, *Anal. Chim. Acta*, **32**, 386 (1965).
6. R. P. Agarwala and M. C. Naik, *Anal. Chim. Acta*, **24**, 128 (1961).
7. L. Reich, *J. Appl. Polymer Sci.*, **10**, 813 (1966).

- S. R. L. Reed, L. Weber, and B. S. Gottfried, *Ind. Eng. Chem. Fundamentals*, **4**, 38 (1965).
9. L. Reich, *J. Inorg. Nucl. Chem.*, **28**, 1329 (1966).
10. R. Tsuchiya, *J. Chem. Soc. (Japan)*, **74**, 16 (1953).
11. D. A. Anderson and E. S. Freeman, *J. Polymer Sci.*, **54**, 253 (1961).

LEO REICH

Polymer Research Branch  
Picatinny Arsenal  
Dover, New Jersey

Received April 11, 1966