APPLICATION OF FIRST ORDER KINETIC EQUATION FOR THE EVALUATION OF KINETIC PARAMETERS BY DTA-URANYL OXALATE TRIHYDRATE SYSTEM

DIFFERENTIAL thermal analysis (DTA) and thermogravimetry (TG) have become important tools in the investigation of solid decomposition reactions. A number of methods[1-5] have been proposed for the evaluation of kinetic parameters using a lumped parameter model of the heat transfer process and assuming that the Arrhenius rate equation is applicable. The assumptions of Borchardt and Daniels are valid only for stirred solutions as has been shown by Reed *et al.*[6] and Mellings *et al.*[7] from a detailed mathematical study of DTA curves. It was however shown in our earlier paper[8] that the first order kinetic equation could be applied successfully for the determination of activation energy for the decomposition of sodium bicarbonate. This method has been extended to the study of the initial dehydration of uranyl oxalate trihydrate.

The apparatus for DTA has been described earlier[9]. Uranyl oxalate trihydrate was prepared by the method of Buttress and Hughes[10] and the composition was confirmed by analysis. Experiments were carried out in large platinum sample holders with the weight of the sample ranging from 80–130 mg.

Padmanabhan *et al.*[11] and Buttress and Hughes (*loc. cit.*) have studied both by DTA and TG the decomposition of this system. Some typical DTA peaks of uranyl oxalate trihydrate obtained at heating rates of 6, 12 and 18° C/min. are given in Fig. 1. The DTA peaks consist of two endotherms representing the loss of two moles and one mole of water respectively and an exotherm consisting of three close-lying kinks corresponding to the decarboxylation of uranium oxalate.

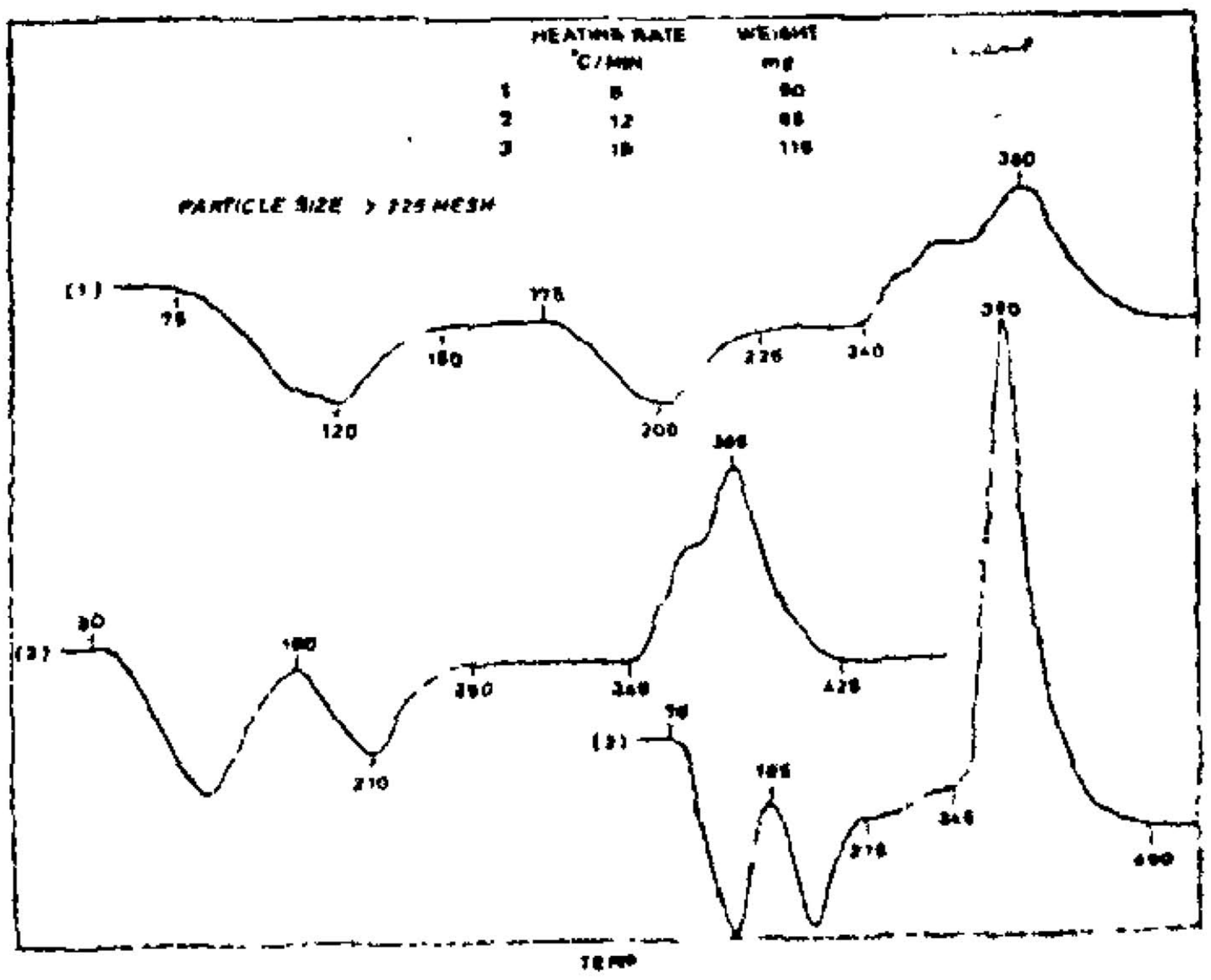

FIG. 1. Some typical DTA peaks of $UO_2C_2O_4 \cdot 3H_2O$ at different heating rates.

The energy of activation was calculated for the initial dehydration step by the use of the first order kinetic equation on the basis of the proportionality of the peak area, A, to the initial amount of the sample and the area, *a*, swept at time, *t*, to the amount decomposed at that time. The rate constant, k, is given by

$$k = \frac{1}{t} \ln \frac{A}{A-a}.$$

The Arrhenius plots are given in Fig. 2 and from the slope of the line the energy of activation has been calculated. The values (Table I) are in good agreement with those reported earlier from thermogravimetric studies and by DTA using the method of Borchardt and Daniels. The values were found to be independent of the rate of heating as was observed in the case of sodium bicarbonate.

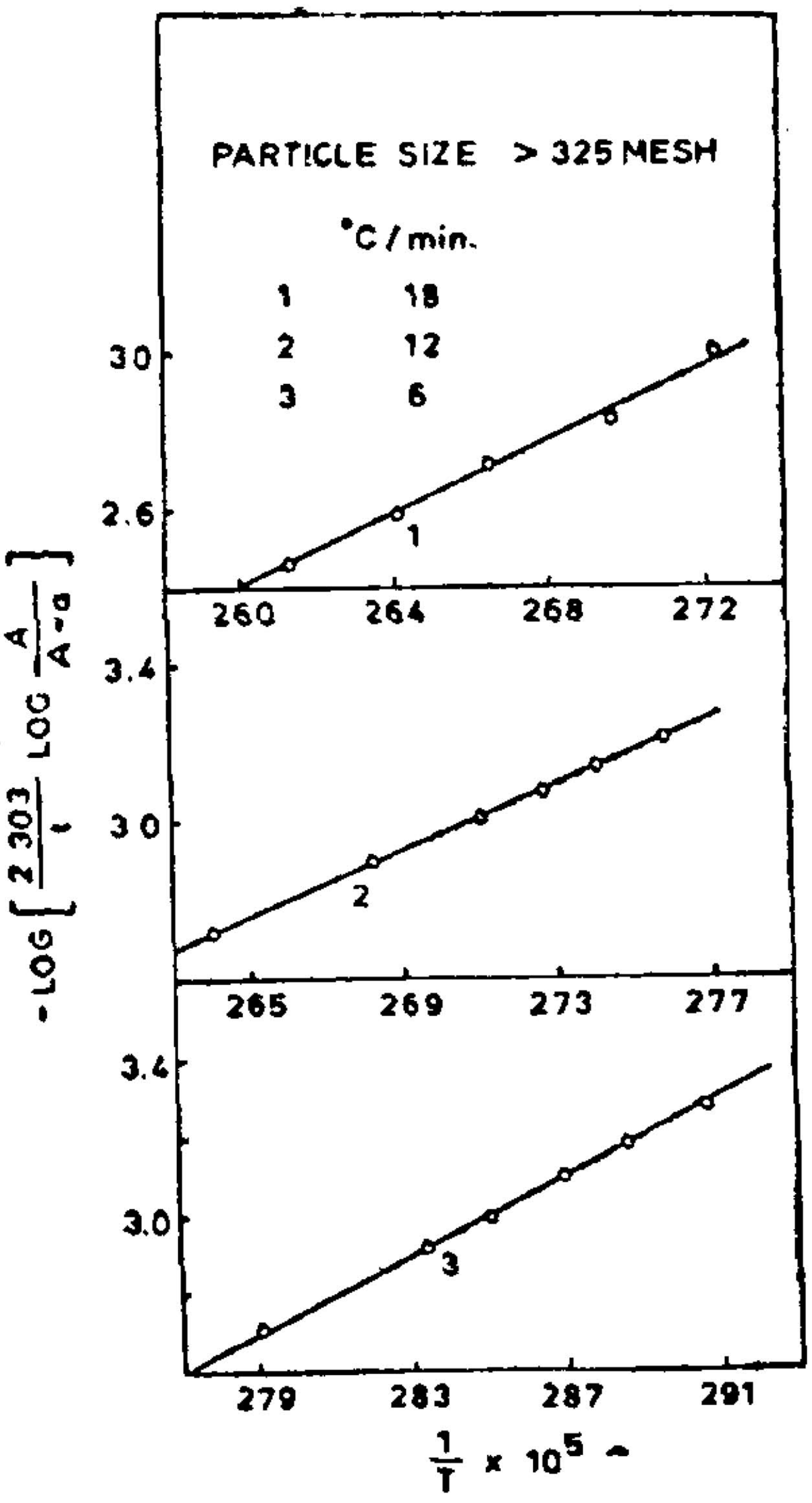

FIG. 2. Arrhenius plots

TABLE I

Values of E for the first step of dehydration of $UO_2C_2O_4 \cdot 3H_2O$

Heating Rate °C/min.	E k.cal/mole	Literature value DTA	Literature value TG
6	22±2	22(11)	19(11)
12	21±1		
18	22±1		

The activation energy calculated both by TG and DTA studies agree well and confirm the applicability of the first order kinetic equation for the evaluation of the kinetic parameters by DTA technique.

Analytical Chemistry
Division,
Bhabha Atomic Research
Centre,
Trombay, Bombay-58,
December 8, 1972.

K. S. SUBRAMANIAN.
T. P. RADHAKRISHNAN.
A. K. SUNDARAM.

---

1. Borchardt, H. J. and Daniels, F., *Jour. Amer. Chem. Soc.*, 1957, 79, 41.
2. Kissinger, H. E., *Anal. Chem.*, 1957, 29, 1702.
3. Reich, L., *J. Inorg. Nuclear Chem.*, 1966, 28, 1329.
4. Freeman, E. S. and Carroll, B., *J. Phys. Chem.*, 1958, 62, 394.
5. Coats, A. W. and Redfern, J. P., *Nature*, 1964, 201, 68.
6. Reed, R. L., Weber, L. and Gottfried, B. S., *Ind. Eng. Chem., Fundamentals*, 1965, 4, 38.
7. Melling. R., Wilburn, F. W. and McIntosh, R. M., *Anal. Chem.*, 1969, 41, 1275.
8. Subramanian, K. S., Radhakrishnan, T. P. and Sundaram, A. K., *Jour. Thermal Analysis*, 1972, 4, 89.
9. —, *B.A.R.C.*, Report-429, 1969.
10. Buttress, G. D. and Hughes, M. H., *J. Chem. Soc.*, 1968, p. 1985.
11. Padmanabhan, V. M., Saraiya, S. C. and Sundaram, A. K., *J. Inorg. Nuclear Chem.*, 1960, 12, 356.