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DETERMINATION OF SOME KINETIC PARAMETERS OF THE THERMAL DECOMPOSITION OF ALKALI PERSULFATES FROM DTA CURVES

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ABSTRACT

Using the DTA curves the thermal decomposition of alkali persulfates for the corresponding pyrosulfates is shown to be a second order reaction with activation energies of 72.7–75.6 kcal mol^{-1} for sodium persulfate and 67.7–69.1 kcal mol^{-1} for potassium persulfate.

INTRODUCTION

In a previous communication[1] the kinetic parameters were determined from the thermogravimetric curves for the thermal decomposition of sodium persulfate applying the Freeman–Carroll method[2]. However, the method was not suitable to estimate the kinetic parameters of potassium persulfate decomposition since the decomposition reaction proceeds rapidly in the temperature range involved.

In this work the DTA curves are utilized for the estimation of the activation energies, E, and the reaction order, n, for the thermal decomposition of sodium and potassium persulfates into the corresponding pyrosulfates applying the Reich expression[3].

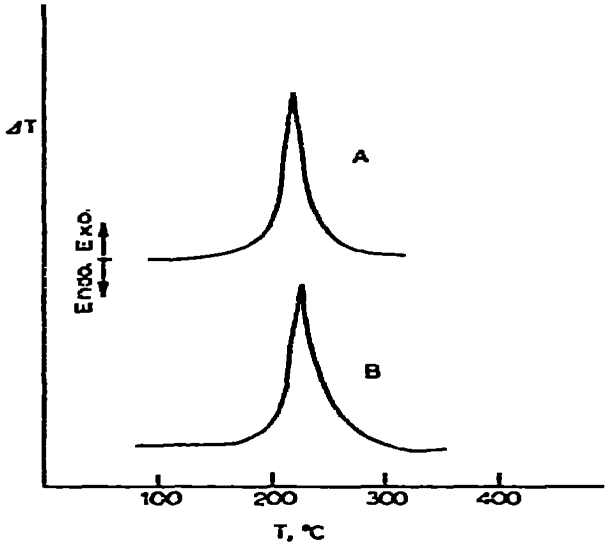
EXPERIMENTAL

The materials used were analytical grade: $Na_2S_2O_8$ and $K_2S_2O_8$ (Hopkin & Williams Analar).

The DTA measurements were carried out in a Paulik–Paulik–Erdey MOM derivatograph under static (air) atmosphere. Samples weighing 200, 250, or 400 mg of the predried compounds were placed in platinum crucibles and heated at 5 and 10°C min^{-1}. α-Al_2O_3 was used as a reference substance. The DTA galvanometer was set on a sensitivity of 1/10 for the 200 and 250 mg samples, and on 1/20 for the 400 mg samples for either heating rates used.

RESULTS AND DISCUSSION

Figures 1 and 2 show the DTA curves of the thermal decomposition of sodium and potassium persulfates into the pyrosulfates, respectively.



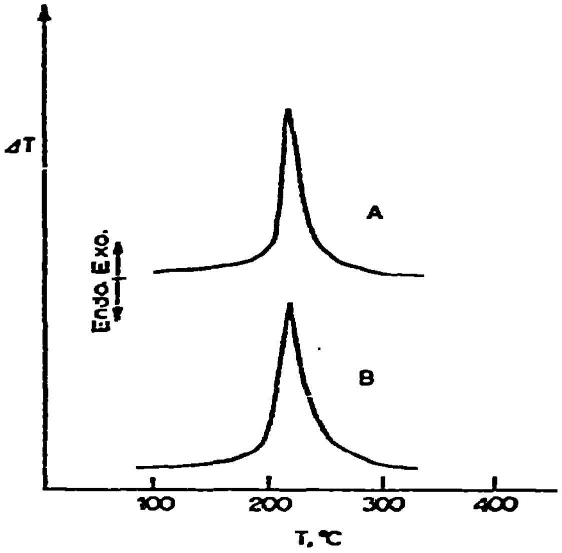


Fig. 1. The DTA curves of sodium persulfate heated at 5°C min^{-1} (A); and at 10°C min^{-1} (B).

Fig. 2. The DTA curves of potassium persulfate heated at 5°C min^{-1} (A); and at 10°C min^{-1} (B).

Reich[3] has introduced a method by which both values E and n can be estimated. By employing the Arrhenius expression, and $\mathrm{d}t = \mathrm{d}T/\mathrm{RH}$, (where t is time elapsed; T the temperature; and RH is the heating rate used) the following relation could be obtained

$$\log\left[\frac{\Delta T(\mathrm{RH})}{A_T}\right] = n\log\frac{\tilde{a}_T}{A_T} - E/2.3RT + K \qquad (1)$$

here ΔT is the height of the DTA curve,

$$A_T = \int_{T_i}^{T_\infty} \Delta T\mathrm{d}T,\; \tilde{a}_T = \int_{T_i}^{T_\infty} \Delta T\mathrm{d}t - \int_{T_i}^{T} \Delta T\mathrm{d}T$$

and K is a function of the initial weight, reaction order, and frequency factor. By employing a "delta" method for two DTA traces of the same substance at two different (RH)s, eqn (1) becomes for a particular temperature

$$\log\left[\left(\frac{\Delta T}{A_T}\right)_1\left(\frac{A_T}{\Delta T}\right)_2\right] = n\log\left[\left(\frac{\tilde{a}_T}{A_T}\right)_1\left(\frac{A_T}{\tilde{a}_T}\right)_2\right] + \log\frac{(\mathrm{RH})_2}{(\mathrm{RH})_1} \qquad (2)$$

where the subscripts 1 and 2 refer to values obtained from DTA traces at $(RH)_1$ and $(RH)_2$, respectively. The value of *n* could be calculated as the slope of the plot of

$$\log\left[\left(\frac{\Delta T}{A_T}\right)_1\left(\frac{A_T}{\Delta T}\right)_2\right] \text{ against } \log\left[\left(\frac{\bar{a}_T}{A_T}\right)_1\left(\frac{A_T}{\bar{a}_T}\right)_2\right]$$

E could be obtained from eqn (1) by substituting the value of n.

In the present case, the plot of eqn (2) was not satisfactory in giving values of *n* in agreement with those reported[1]. So values of 1.8, 2.0, 2.15, and 2.3 were assumed for the reaction order. According to eqn (1), the term

$$n\log\left(-\frac{A_T}{\bar{a}_T}\right) - \log\left(\frac{A_T}{\Delta T}\right)$$

was plotted against $1/T$ for the two heating rates used (Figs. 3–6).

The values of activation energies obtained for the decomposition reactions are listed in Table 1.

It is obvious that, for *n* equals 2 the values of *E* obtained at the two heating rates are closest to each other and in more agreement with the values obtained by Barbooti and Jasim[1].

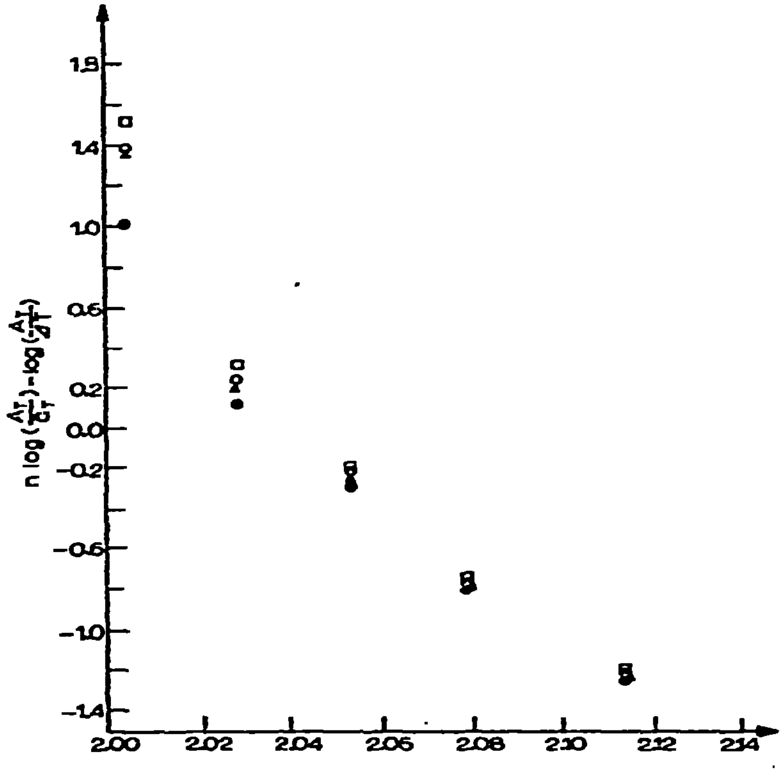


Fig. 3. The plots of eq. (1) for sodium persulfate heated at 5°C min^{-1} for reaction order, *n*, of 1.8, ●; 2.0, △; 2.15, ○; and 2.3, □.

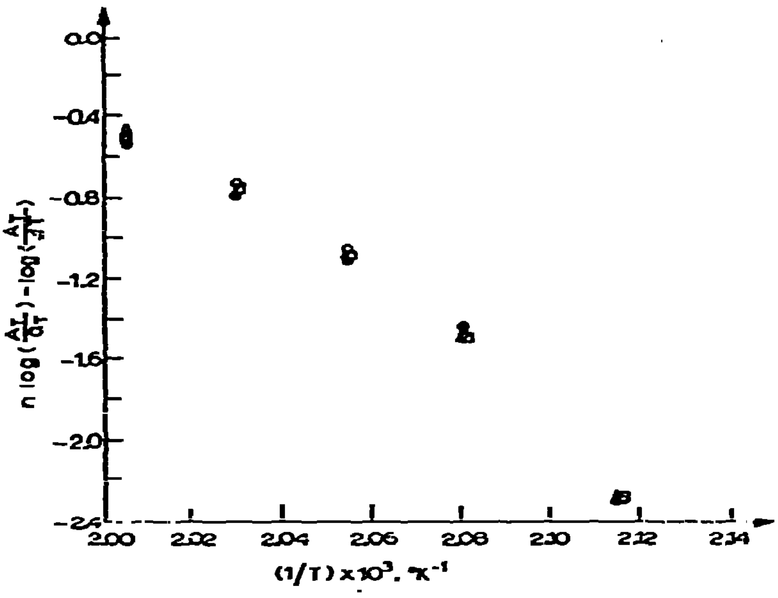


Fig. 4. The plots of eq. (1) for sodium persulfate heated at 10°C min⁻¹ for reaction order, *n*, of 1.8, ●; 2.0, △; 2.15, ○; and 2.3, □.

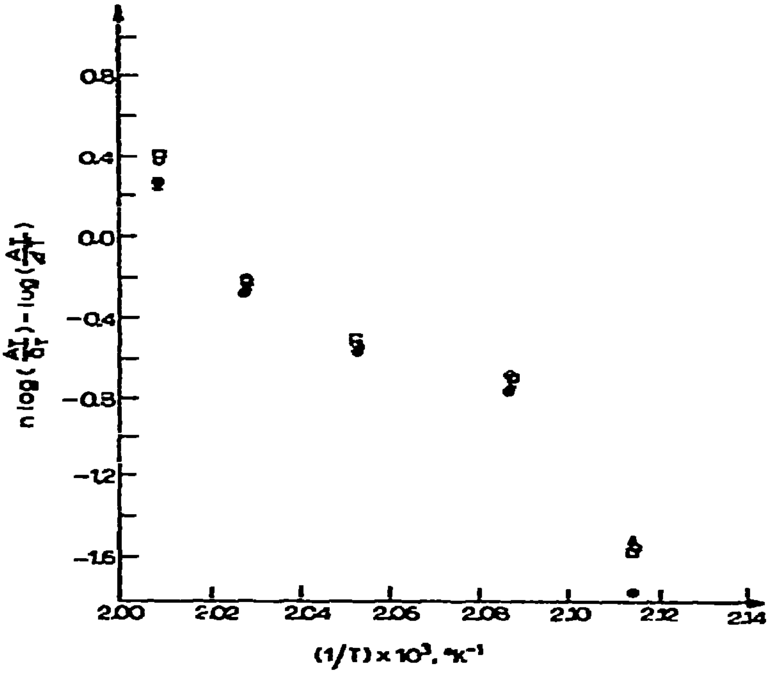


Fig. 5. The plots of eq. (1) for potassium persulfate heated at 5°C min⁻¹ for reaction order, *n*, of 1.8, ●; 2.0, △; 2.15, ○; and 2.3, □.

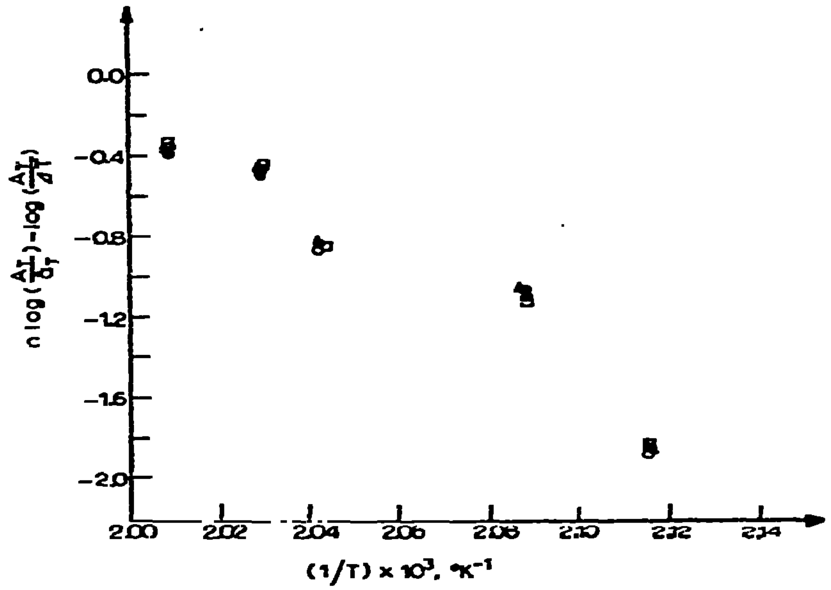


Fig. 6. The plots of eq. (1) for potassium persulfate heated at 10°C min^{-1} for reaction order, *n*, of 1.8, ●; 2.0, △; 2.15, ○; and 2.3, □.

TABLE 1

THE ACTIVATION ENERGIES OBTAINED FOR SODIUM AND POTASSIUM PERSULFATES

Material	*Heating rate (°C min^{-1})*	*Activation energy*^{a} *(kcal mol^{-1})*			
		Reaction order			
		1.8	*2.0*	*2.15*	*2.3*
$Na_2S_2O_8$	5	73.7	75.6	76.0	82.9
	10	70.8	72.7	65.2	62.4
$K_2S_2O_8$	5	76.6	69.1	70.3	80.6
	10	67.0	67.7	65.6	63.1

^{a} The values are taken for the 200 mg samples.

CONCLUSION

The estimation of the kinetic parameters from the DTA curves is dependent to a certain limit on the heating rate used. However, plots similar to those of Figs. 3–6 were obtained from DTA traces for samples weighing 250 and 400 mg. This indicates the independence of *E* on the sample weight analysed.

The thermal decomposition reactions

$$Na_2S_2O_8 \xrightarrow{\Delta} Na_2S_2O_7 + \tfrac{1}{2}O_2$$

$$K_2S_2O_8 \xrightarrow{\Delta} K_2S_2O_7 + \tfrac{1}{2}O_2$$

therefore, are second order reactions with activation energies in the range of 72.7–75.6 kcal mol^{-1} for $Na_2S_2O_8$ and 67.7–69.1 kcal mol^{-1} for $K_2S_2O_8$.

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