

## The kinetics and mechanism of induced thermal decomposition of peroxomonosulphate by phase transfer catalysts

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**Abstract.** The kinetics of induced decomposition of potassium peroxomonosulphate (PMS) by the phase transfer catalysts (PTC), viz. tetrabutylammonium chloride [TBAC] and tetrabutylphosphonium chloride [TBPC] have been investigated. The effect of [PMS], [PTC], ionic strength of the medium and temperature on the rate of decomposition of PMS was studied. The rate of decomposition of PMS was monitored under pseudo-first-order condition at a constant temperature ( $50 \pm 0.1^\circ\text{C}$ ). The rate of decomposition was first order with respect to PMS for TBAC and half order for TBPC. The order with respect of PTC was found to be unity for TBAC and half order for TBPC. A suitable kinetic scheme has been proposed to account for the experimental data and its significance is discussed.

**Keywords.** Thermal decomposition; potassium peroxomonosulphate; phase transfer catalysts.

### 1. Introduction

Phase transfer catalysis is a potent and versatile synthetic tool and has been employed not only in organic chemistry<sup>1</sup> but also in inorganic chemistry<sup>2</sup>, analytical application<sup>3</sup>, in electrochemistry<sup>4–7</sup>, photochemistry<sup>8,9</sup> and in polymer chemistry<sup>10–15</sup>.

The spontaneous decomposition of potassium peroxomonosulphate (PMS) in aqueous solution suggests that free radicals are not formed. The kinetics and mechanism of the aqueous decomposition of Caro's acid was investigated by Ball and Edwards<sup>16,17</sup>. The oxidant undergoes both spontaneous and catalytic decomposition in acidic and alkaline media. The products of thermal decomposition are identified as oxygen and sulphate ions. The decomposition is found to be second order in total [PMS] at  $25^\circ\text{C}$  and exhibits two types of acid dependence, viz. a direct first order dependence on acid concentration in the basic region and an inverse first order dependence on acid concentration in the acidic region.

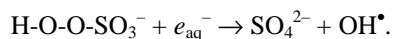
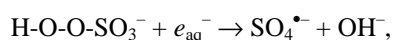
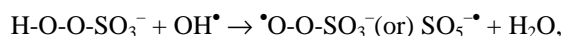
Hence, PMS exists as  $\text{HSO}_5^-$  in the *pH* range 6–8 and only  $\text{SO}_5^{2-}$  in the *pH* range greater than 10.5. Thompson<sup>18</sup> observed that the combination of  $\text{Ag}^+$  and PDS is an active catalyst for the decomposition of PMS and reported first-order dependence on PMS and first-order dependence on the catalyst. Thompson also reported first-order dependence on PMS with cobalt catalyst at *pH*: 0. Mariano<sup>19</sup> reported first-order dependence on PMS in the presence of Ce(IV) catalyst system. Photolytic decomposition

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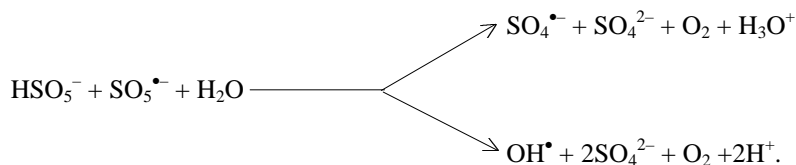
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of potassium peroxomonosulphate was carried out by Kanakaraj and Maruthamuthu<sup>20</sup>. They observed first-order dependence on [PMS] with respect to photolytic exposure. The primary radical products  $\text{SO}_4^{\bullet-}$  and  $\text{OH}^{\bullet}$  are formed by homolytic splitting of PMS. These were identified by syn-trapping agents such as fumaric and maleic acids<sup>21,22</sup>.

Radiolytic decomposition of PMS has been studied extensively<sup>19,22,23</sup>. Energetic radiation produces three reactive species in water ( $\text{H}^{\bullet}$ ,  $\text{OH}^{\bullet}$  and  $e_{\text{aq}}^-$ ). It is inferred that both  $e_{\text{aq}}^-$  and  $\text{OH}^{\bullet}$  are efficient in effecting the decomposition of PMS. The formation of  $\text{SO}_5^{\bullet-}$  as a secondary product has also been suggested as a result of the following reactions:



The formation of  $\text{SO}_5^{\bullet-}$  and  $\text{SO}_4^{\bullet-}$  as the radical products were identified by optical pulse radiolysis<sup>22</sup> and oxygen as a molecular product was identified by mass spectrometry. The reaction responsible for the chain decomposition is the reduction of PMS by  $\text{SO}_5^{\bullet-}$  as follows:



Free radical polymerization of water-soluble monomers and acrylic monomers with potassium peroxydisulphate (PDS) and potassium peroxomonosulphate (PMS) as initiators has been extensively studied in aqueous media<sup>24</sup>. Phase transfer catalyst (PTC)-assisted polymerization reactions have received considerable attention in recent years<sup>25</sup>. In the presence of phase transfer catalyst (PTC), the monomer in the organic phase reacts with the initiator (PMS/PDS) in the aqueous phase. The reaction is achieved by means of PTC which complexes and solubilizes the water-soluble initiator in the organic phase. Both potassium peroxydisulphate and potassium peroxomonosulphate generate free radicals by scission of the peroxide bond (-O-O-), which might initiate the polymerization of acrylic monomers. Phase transfer catalysis is not limited to studies involving free radicals, but also encompasses reactions with anions, cations, whole molecules or even energy (chemical form).

In our primary objective to study the free radical polymerization of vinyl monomers in the presence of PMS assisted by phase transfer catalysts, we found that the induced decomposition of potassium peroxomonosulphate by phase transfer catalyst in aqueous solution in the presence of quaternary ammonium and phosphonium salts have not been reported so far. Hence, the present investigation deals with the decomposition of PMS in aqueous solution induced by TBAC and TBPC and the importance of phase transfer catalyst coupled with PMS for generating free radicals, viz.  $\text{SO}_4^{\bullet-}$  and  $\text{OH}^{\bullet}$ .

## 2. Experimental

### 2.1 Reagents and chemicals

Potassium peroxomonosulphate was obtained from EI Dupont Company, USA, as Oxone<sup>26</sup>, a mixture of composition  $2\text{KHSO}_5\text{KHSO}_4\text{K}_2\text{SO}_4$ . Solutions of this salt were assayed iodometrically and by cerimetry and the purity was 96%. No further purification was attempted because of the difficulties reported by the earlier workers<sup>22</sup>. Phase transfer catalysts, viz. tetrabutylammonium chloride (TBAC, Fluka) and tetrabutyl phosphonium chloride (TBPC, Fluka), were used as such. Other chemicals such as potassium iodide (E Merck), sulphuric acid, sodium acetate and acetic acid (AR, CDH) were purchased from local stores and used as such.

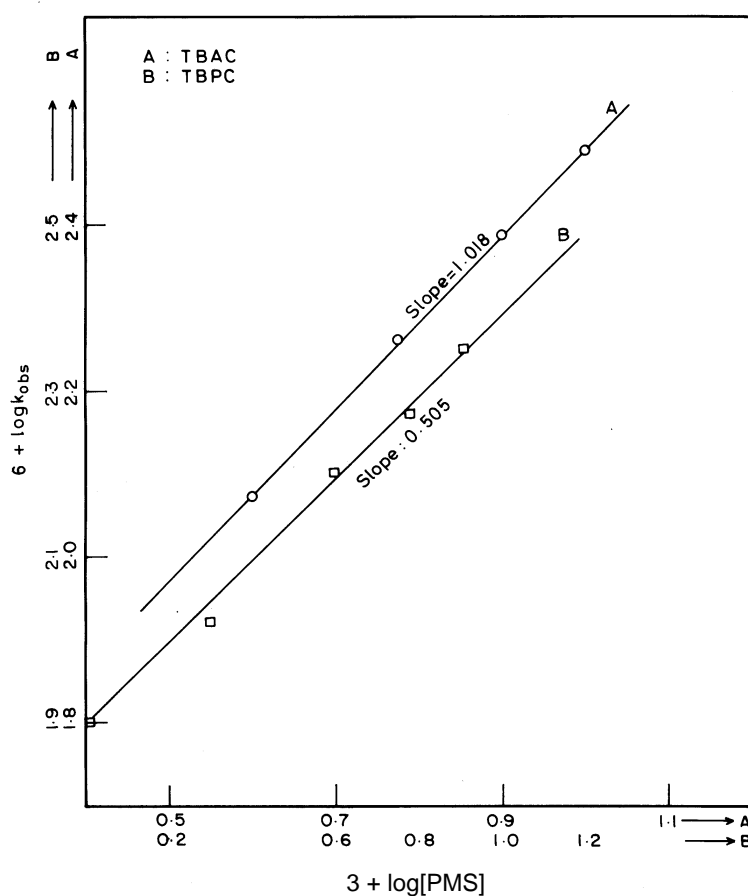
Induced thermal decomposition of PMS experiments were carried out in a thermostatic water-bath of 20 litres capacity and the water-bath was heated electrically and stirred well by a mechanical stirrer to maintain constant temperature with an accuracy of  $\pm 0.1^\circ\text{C}$ . The reaction mixture was kept at  $50 \pm 0.1^\circ\text{C}$  and a calculated volume of PMS was pipetted out into the reaction mixture containing the calculated quantity of PTC, buffer ( $\text{pH}$ : 4.0) and potassium hydrogen sulphate ( $0.075 \text{ mol dm}^{-3}$ ). The reaction mixture (5 ml) was withdrawn at known intervals of time and transferred quantitatively into a conical flask containing approximately 20 ml of ice cold 0.1 N sulphuric acid and to this 10 ml of 5% potassium iodide solution was added. The liberated iodine was titrated against standard sodium thiosulphate using starch as the indicator. Unreacted potassium peroxomonosulphate concentration was determined iodometrically for each reaction. The pseudo-first order rate constant  $k_{\text{obs}}$  was evaluated from the slopes of the plots of  $\log [\text{PMS}]_t$  vs time. The decomposition of PMS experiments were also carried out at different temperatures in the range  $40\text{--}55^\circ\text{C}$  to evaluate the thermodynamic parameters.

## 3. Results and discussion

The decomposition experiments were carried out under pseudo-first-order conditions at constant  $\text{pH}$  (4.0) and ionic strength  $0.075 \text{ mol dm}^{-3}$  at  $50 \pm 0.1^\circ\text{C}$  keeping  $[\text{TBAC}]$   $[\text{PMS}]$  in the case of the study of the effect of  $[\text{PMS}]$  and  $[\text{PMS}]$   $[\text{TBAC}]$  when studying the effect of  $[\text{TBAC}]$  on the decomposition of PMS. Similar experimental conditions were adopted for the TBPC and PMS systems. At fixed concentration of TBAC and other experimental parameters, increase of  $[\text{PMS}]$  increases the decomposition rate of PMS. A plot of  $k_{\text{obs}}$  vs  $\log[\text{PMS}]$  gives a straight line with a slope equal to unity (figure 1). A plot of  $k_{\text{obs}}$  vs  $[\text{PMS}]^{1.0}$  gives a straight line passing through the origin, thus supporting first-order dependence on  $[\text{PMS}]$ . Under identical experimental conditions, we have studied the catalytic effect of TBPC and found half-order dependence on PMS. A plot of  $k_{\text{obs}}$  vs  $[\text{PMS}]^{0.5}$  is linear and passes through the origin supporting the above order dependence on  $[\text{PMS}]$ .

At fixed  $[\text{PMS}]$  and other parameters, increase of  $[\text{TBAC}]$  increases the decomposition rate. A plot of  $\log k_{\text{obs}}$  vs  $\log [\text{TBAC}]$  gives a straight line and the slope is found to be unity (figure 2). Plots of  $k_{\text{obs}}$  vs  $[\text{TBAC}]$  give straight lines passing through the origin thereby confirming first-order dependence of rate on  $[\text{TBAC}]$ . Therefore the decomposition with phase transfer catalyst follows total second-order kinetics, first-order each with respect to  $[\text{PMS}]$  and  $[\text{TBAC}]$ . Under identical experimental conditions, we

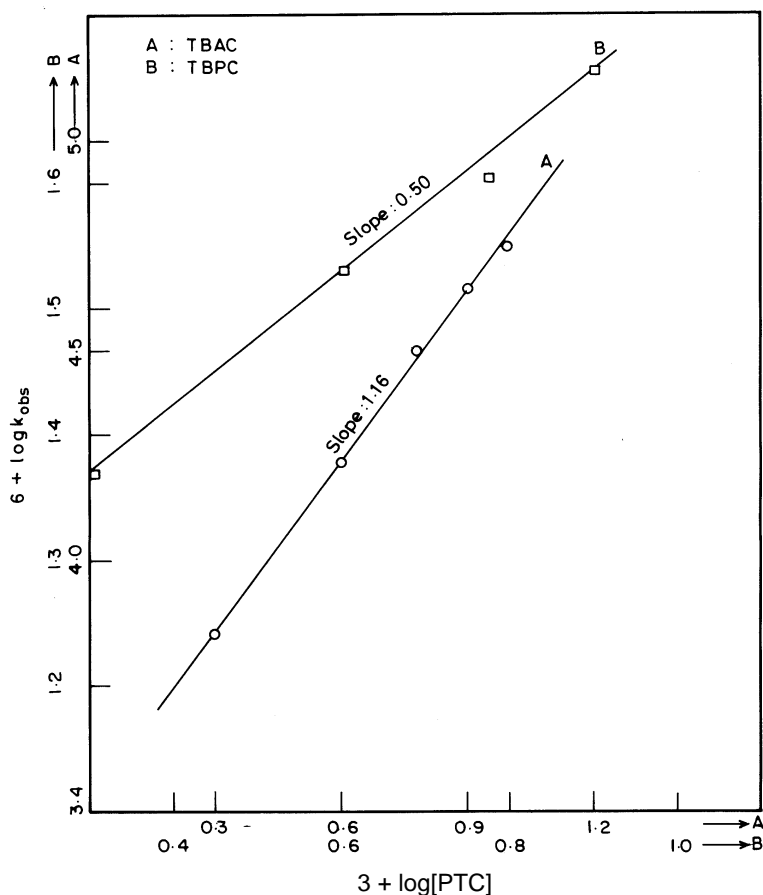
observed half-order dependence on [TBPC]. A plot of  $k_{\text{obs}}$  vs  $[\text{TBPC}]^{0.5}$  is linear and passes through the origin supporting the above order dependence. Thus the decomposition kinetics of PMS by TBPC can be explained based on the stoichiometric ratios of the formation of the ion-pair (or) intermediate complex of PMS and TBPC. A similar trend is observed in the kinetics and free radical polymerization of acrylonitrile initiated by phase transfer catalysts (TBAC/TBPC) coupled with potassium peroxomonosulphate. Decomposition experiments were also carried out at different ionic strengths ( $0.065\text{--}0.085\text{ mol dm}^{-3}$ ). The variation of ionic strength has a negligible effect on the reaction rates. The pseudo unimolecular rate constants for the decomposition of PMS and Michaelis constants for TBAC and TBPC are presented in table 1.



**Figure 1.** Decomposition of PMS in presence of TBAC/TBPC, variation of [PMS].

**Table 1.** Decomposition of PMS: Michaelis and decomposition rate constants.

Catalyst	$k_2$ ( $\text{l mol}^{-1} \text{s}^{-1}$ )	$K_m$ (M)
TBAC	$4.26 \times 10^{-3}$	$1.47 \times 10^{-2}$
TBPC	$2.72 \times 10^{-4}$	$2.49 \times 10^{-3}$



**Figure 2.** Decomposition of PMS in presence of TBAC/TBPC, variation of [PTC].

**Table 2.** Decomposition of PMS: Thermodynamic and activation parameters.

Catalyst	$E_a$ (kcal mol <sup>-1</sup> )	$A \times 10^{16}$ (l mol <sup>-1</sup> s <sup>-1</sup> )	$\Delta H^\ddagger$ (kcal mol <sup>-1</sup> )	$\Delta S^\ddagger$ (cal K <sup>-1</sup> mol <sup>-1</sup> )	$\Delta G^\ddagger$ (kcal mol <sup>-1</sup> )
TBAC	21.4	4.20	21.2	-64.3	26.2
TBPC	30.8	2.76	30.2	-14.6	26.1

### 3.1 Effect of temperature

The effect of temperature on the decomposition of PMS was studied in the range of 45–55 ± 0.1°C, while keeping the other parameters constant. An increase in the rate of decomposition of PMS with increase in temperature is observed. The energy of activation ( $E_a$ ) for the induced decomposition of PMS by phase transfer catalysts are calculated from the Arrhenius plot (figure 4). The thermodynamic parameters are calculated and presented in table 2.

Based on the available data on PTC-induced decomposition of PMS and on the mechanism reported in the literature for other catalysed reactions, the following mechanism is proposed.



where  $Q^+$  is tetrabutyl ammonium (or) tetrabutyl phosphonium ion,



Applying the steady state approximation for the complex shown by Briggs and Haldane<sup>27,28</sup>

$$k_1[Q^+][HSO_5^-] - k_{-1}[Q^+HSO_5^-] - k_2[Q^+HSO_5^-] = 0. \quad (3)$$

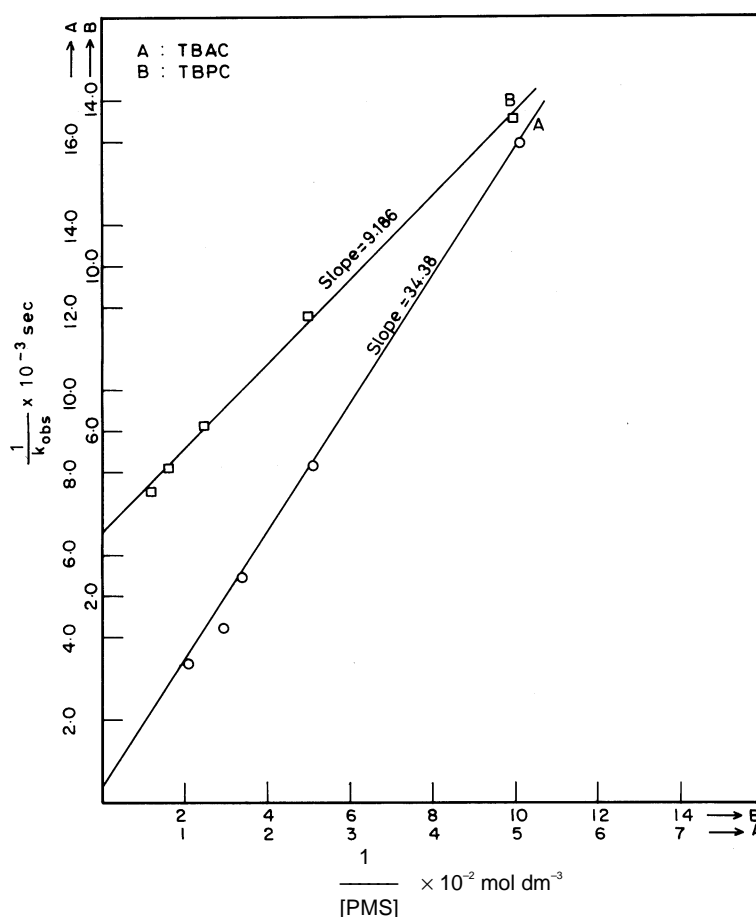


Figure 3. Decomposition of PMS in presence of TBAC/TBPC.

The total concentration of the catalyst  $[Q^+]_{total}$  is equal to the concentration of the catalyst unreacted  $[Q^+]$  and the concentration of the complex  $[Q^+HSO_5^-]$ ,

$$[Q^+]_{total} = [Q^+]_{(w)} + [Q^+HSO_5^-]_{(w)}. \quad (4)$$

Rearranging the above equation, gives

$$[Q^+]_{(w)} = [Q^+]_{total} - [Q^+HSO_5^-]_{(w)}. \quad (5)$$

Substituting for  $[Q^+]_{(w)}$  from (5) into (3)

$$k_1\{[Q^+]_{total} - [Q^+HSO_5^-]\}[HSO_5^-] - [k_{-1} + k_2][Q^+HSO_5^-] = 0. \quad (6)$$

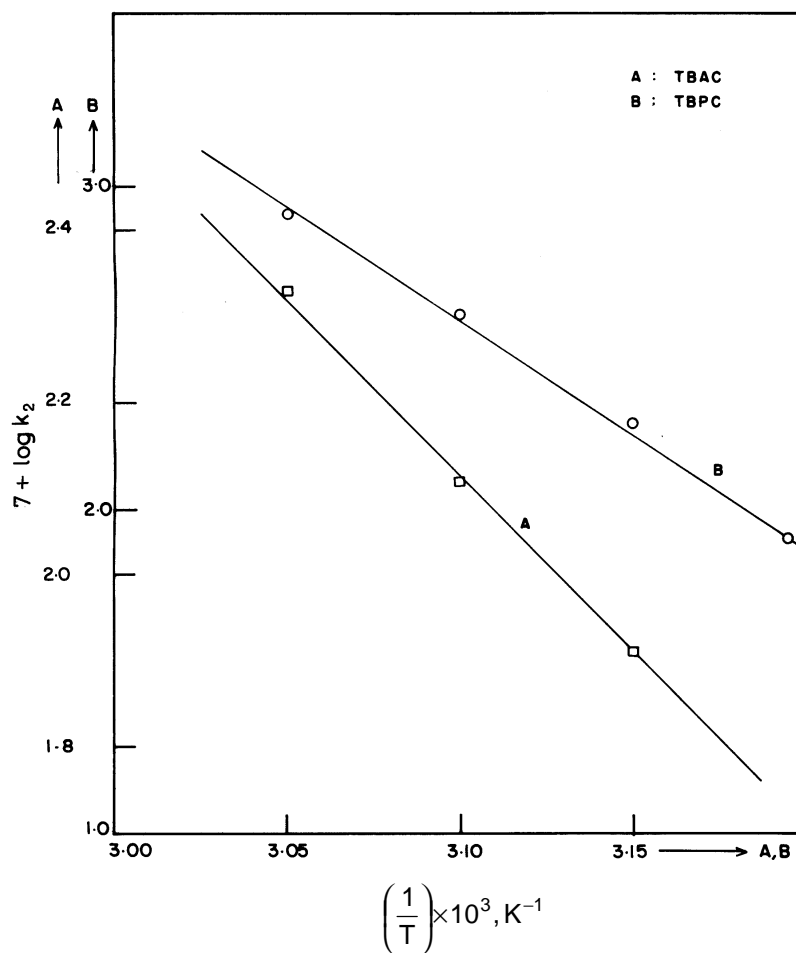


Figure 4. Decomposition of PMP in presence of PTC, temperature variation.

Hence

$$[\text{Q}^+\text{HSO}_5^-] = k_1[\text{Q}^+]_{\text{total}} [\text{HSO}_5^-]_{(w)}/(k_{-1} + k_2 + k_1 [\text{HSO}_5^-]_{(w)}). \quad (7)$$

The rate of decomposition of PMS is therefore,

$$-d[\text{PMS}]/dt = \mathbf{u} = k_2 [\text{Q}^+\text{HSO}_5^-]. \quad (8)$$

Substituting  $[\text{Q}^+\text{HSO}_5^-]$  from (7) into (8) we get,

$$\mathbf{u} = k_1 k_2 [\text{Q}^+]_{\text{total}} [\text{HSO}_5^-]_{(w)}/(k_{-1} + k_2 + k_1 [\text{HSO}_5^-]_{(w)}). \quad (9)$$

Dividing by  $k_1$ , (9) becomes

$$\mathbf{u} = k_2 [\text{Q}^+]_{\text{total}} [\text{HSO}_5^-]_{(w)} \left( \frac{k_1 + k_2}{k_1} \right) + [\text{HSO}_5^-]_{(w)}, \quad (10)$$

$$\mathbf{u} = k_2 [\text{Q}^+]_{\text{total}} [\text{HSO}_5^-]_{(w)} / K_m + [\text{HSO}_5^-]_{(w)}, \quad (11)$$

where  $K_m = (k_{-1} + k_2)/k_1$ , is the Michaelis constant.

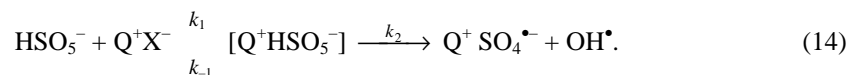
The values of  $K_m$  and  $k_2$  are calculated from the slope and intercept of the plot of  $1/k_{\text{obs}}$  versus  $1/[\text{PMS}]$  (figure 3, table 1) respectively.

If  $[\text{HSO}_5^-]$  is sufficiently small, (11) becomes

$$\mathbf{u} = (k_2/K_m) [\text{Q}^+]_{\text{total}} [\text{HSO}_5^-]_{(w)}, \quad (12)$$

so that the order with respect to  $[\text{PMS}]$  and  $[\text{PTC}]$  is unity. If  $K_m$  is greater than  $[\text{HSO}_5^-]_{(w)}$ , then the order with respect to  $[\text{PMS}]$  and  $[\text{PTC}]$  is half.

Thus PTC-induced decomposition of PMS suggests that the PMS decomposes into sulphate radical anion, ( $\text{SO}_4^{\bullet-}$ ) and hydroxyl free radical, ( $\text{OH}^\bullet$ ). PMS exists as  $\text{HSO}_5^-$  in aqueous solution in the absence of high acidity and alkalinity<sup>16</sup>. Unlike the symmetrical peroxydisulphate ( $\text{S}_2\text{O}_8^{2-}$ ), which gives two sulphate ion radicals on homolytic fission, PMS gives  $\text{SO}_4^{\bullet-}$  and  $\text{OH}^\bullet$  radicals,



#### 4. Conclusions

The rate constant for the decomposition of PMS in the presence of phase transfer catalysts, TBAC and TBPC, is given in table 1. It is observed that PMS decomposes fifteen times faster in the presence of TBAC compared to its decomposition in the presence of TBPC. This is also supported by the higher energy of activation (table 2) and  $K_m$  values. Table 1 suggests that the disappearance of the PMS–TBAC complex is much



faster compared to that of PMS–TBPC complex. It is therefore concluded that  $[\text{Bu}_4\text{N}^+ \text{HSO}_5^-]$  is more reactive in initiating the polymerization and, in fact, this is also observed in reality<sup>29</sup>.

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