

## The Effect of Hydrogen Peroxide Vapour on the Decomposition of Perhydrates

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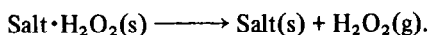
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Our recent investigations of the thermal decomposition of perhydrates clearly demonstrated that the mechanism is closely related to the decomposition of hydrates. Firstly, hydrogen peroxide can be detected in the vapour above heated perhydrates [1]. Secondly, the pyrolysis of alkali metal oxalate perhydrates and hydrates follow similar kinetic laws [2]. There is thus considerable evidence that the key steps in the decomposition of perhydrates at elevated temperatures is the following dissociation:



A necessary consequence of this mechanism is that the presence of  $\text{H}_2\text{O}_2$  vapour should retard the

decomposition of perhydrates, just as hydrates are stabilized by humidity in the atmosphere. For experimental reasons this hypothesis is difficult to test in the pyrolysis of perhydrates, but proved easy to apply to the decomposition of perhydrates at room temperature. The latter exercise is the subject of this paper.

We have noted elsewhere that the rate of decomposition of perhydrate at room temperature generally depends on the humidity [1]. Two types of behaviour are observed.

(1) The rate of decomposition is smoothly dependent on humidity (curve 1 in Fig. 1).

(2) The rate of decomposition markedly increases at a critical relative humidity (Curve 2 in Fig. 1).

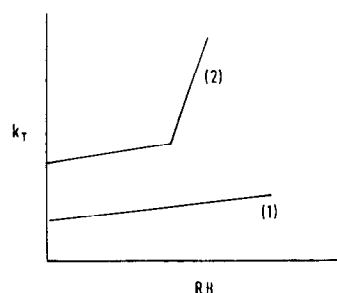


Fig. 1. Dependence of rate constant on relative humidity (RH) in perhydrate decompositions.

TABLE I. Experimental Details.

Compound	T/°C	Experimental Atmosphere			Control Atmosphere	
		PH <sub>2</sub> O <sub>2</sub> /mmHg	PH <sub>2</sub> O/mmHg	Source	PH <sub>2</sub> O/mmHg	Source [4]
Na <sub>2</sub> C <sub>2</sub> O <sub>4</sub> ·H <sub>2</sub> O <sub>2</sub>	20	0.52	6.16	50% mol fraction H <sub>2</sub> O <sub>2</sub>	6.14	Saturated CrO <sub>3</sub>
K <sub>2</sub> C <sub>2</sub> O <sub>4</sub> ·H <sub>2</sub> O <sub>2</sub>	20	0.05	15.55	10% mol fraction H <sub>2</sub> O <sub>2</sub>	15.4	Saturated K <sub>2</sub> CrO <sub>4</sub>

TABLE II. Thermodynamics of Oxalate Perhydrate Decomposition.

	ΔH/kJ mol <sup>-1</sup>	ΔS/J mol <sup>-1</sup> K <sup>-1</sup>	ΔG <sub>298</sub> /kJ mol <sup>-1</sup>
K <sub>2</sub> C <sub>2</sub> O <sub>4</sub> ·H <sub>2</sub> O <sub>2</sub> (s) → K <sub>2</sub> C <sub>2</sub> O <sub>4</sub> (s) + H <sub>2</sub> O <sub>2</sub> (g)	86.5 <sup>a</sup>	174.7 <sup>b</sup>	34.3 <sup>d</sup>
K <sub>2</sub> C <sub>2</sub> O <sub>4</sub> (s) + H <sub>2</sub> O(g) → K <sub>2</sub> C <sub>2</sub> O <sub>4</sub> ·H <sub>2</sub> O(s)	-59.0 <sup>a</sup>	-149.4 <sup>c</sup>	-14.5 <sup>d</sup>
K <sub>2</sub> C <sub>2</sub> O <sub>4</sub> ·H <sub>2</sub> O <sub>2</sub> (s) + H <sub>2</sub> O(g) → K <sub>2</sub> C <sub>2</sub> O <sub>4</sub> ·H <sub>2</sub> O(s) + H <sub>2</sub> O <sub>2</sub> (g)	27.5	25.3	19.9 <sup>e</sup>

<sup>a</sup>Data from Ref. [2]. <sup>b</sup>With the assumption that  $S^0(\text{salt} \cdot \text{H}_2\text{O}_2) - S^0(\text{salt}) = 58.2 \text{ J mol}^{-1} \text{ K}^{-1}$  and using  $S^0(\text{H}_2\text{O}_2) = 232.9 \text{ J mol}^{-1} \text{ K}^{-1}$  [5]. <sup>c</sup>With the assumption that  $S^0(\text{salt} \cdot \text{H}_2\text{O}) - S^0(\text{salt}) = 39.3 \text{ J mol}^{-1} \text{ K}^{-1}$  [6] and using  $S^0(\text{H}_2\text{O}) = 188.7 \text{ J mol}^{-1} \text{ K}^{-1}$  [5]. <sup>d</sup>Assuming ΔH is independent of temperature. <sup>e</sup> $\Delta G_{298} = -RT \ln K_p = -RT \ln P_{\text{H}_2\text{O}_2}/P_{\text{H}_2\text{O}}$ .

Decomposition can give either an anhydrous salt or a hydrate. Critical dependence on relative humidity is associated with the formation, on the surface of the solid, of a film of saturated solution.

### Experimental

In view of the complicating factor of relative humidity, the plan of our investigation was as follows. Samples of perhydrates were stored at constant temperature in the presence of hydrogen peroxide solutions of known  $\text{H}_2\text{O}_2$  and  $\text{H}_2\text{O}$  vapour pressure [3]. In control experiments, identical samples were exposed to atmospheres of similar humidity controlled by saturated salt solutions. Two perhydrates were examined:  $\text{Na}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}_2$  which decomposes to the anhydrous oxalate and  $\text{K}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}_2$  which decomposes to the monohydrate. Details of the experiments are given in Table I.

### Results and Discussion

In both cases the rate of decomposition of the solid is dramatically reduced by the presence of low pressures of  $\text{H}_2\text{O}_2$  (Figs. 2 and 3). We can therefore contend that the mechanism of decomposition of perhydrates at room temperature is the same as that at elevated temperature, and that the following equilibria exist:

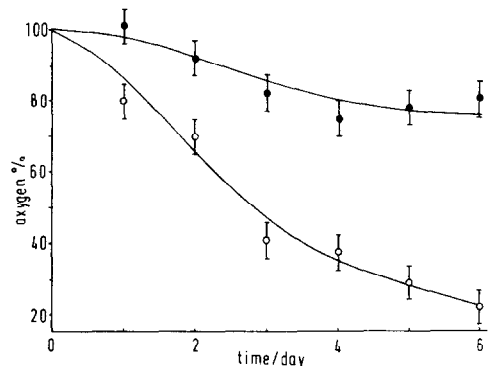
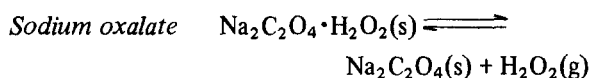


Fig. 2. Decomposition curve for  $\text{Na}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}_2$  as a function of time at 20 °C. Open circles at 35% RH, filled circles at 35% RH and 0.52 mm Hg  $\text{H}_2\text{O}_2$  vapour pressure.

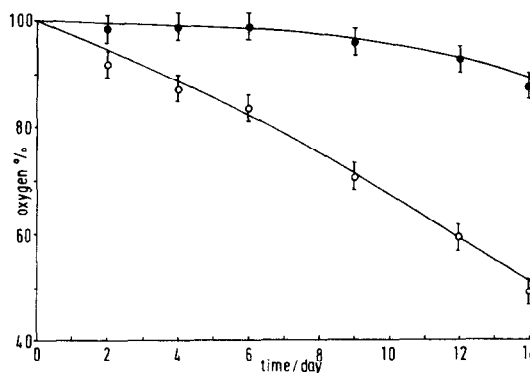
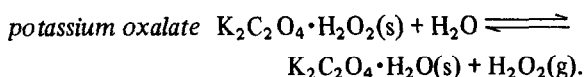


Fig. 3. Decomposition curve for  $\text{K}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}_2$  as a function of time at 20 °C. Open circles at 88% RH, filled circles at 88% RH and 0.05 mm Hg  $\text{H}_2\text{O}_2$  vapour pressure.



Equilibrium constants for these reactions could, in principle, be determined by measuring the pressures of  $\text{H}_2\text{O}_2$  and  $\text{H}_2\text{O}$  in equilibrium over the perhydrates. We can, however, estimate this constant for potassium oxalate from thermochemical data obtained in our earlier investigation of oxalate perhydrates [2] (Table II), where the equilibrium constant at 20 °C is seen to be  $3.2 \times 10^{-4}$ . Hence the pressure of  $\text{H}_2\text{O}_2$  in equilibrium with the potassium oxalate perhydrate is very small (about three thousandth of the water vapour pressure), but it is still sufficient to cause decomposition of the solid at room temperature.

### References

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