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The Effect of Hydrogen Peroxide Vapour on the Decomposition of Perhydrates

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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:

$$\text{Salt}\cdot H_2O_2(s) \longrightarrow \text{Salt}(s) + H_2O_2(g).$$

A necessary consequence of this mechanism is that the presence of H_2O_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).

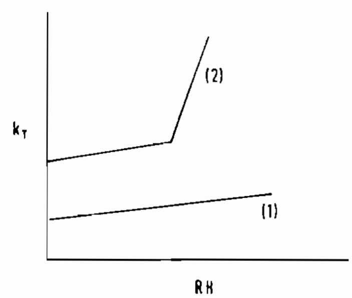

Fig. 1. Dependence of rate constant on relative humidity (RH) in perhydrate decompositions.

TABLE I. Experimental Details.

Compound	T/°C	Experimental Atmosphere			Control Atmosphere	
		PH_2O_2/mmHg	PH_2O/mmHg	Source	PH_2O/mmHg	Source [4]
$Na_2C_2O_4\cdot H_2O_2$	20	0.52	6.16	50% mol fraction H_2O_2	6.14	Saturated CrO_3
$K_2C_2O_4\cdot H_2O_2$	20	0.05	15.55	10% mol fraction H_2O_2	15.4	Saturated K_2CrO_4

TABLE II. Thermodynamics of Oxalate Perhydrate Decomposition.

	ΔH/kJ mol^{-1}	ΔS/J mol^{-1} K^{-1}	ΔG$_{298}$/KJ mol^{-1}
$K_2C_2O_4\cdot H_2O_2(s) \rightarrow K_2C_2O_4(s) + H_2O_2(g)$	86.5[a]	174.7[b]	34.3[d]
$K_2C_2O_4(s) + H_2O(g) \rightarrow K_2C_2O_4\cdot H_2O(s)$	−59.0[a]	−149.4[c]	−14.5[d]
$K_2C_2O_4\cdot H_2O_2(s) + H_2O(g) \rightarrow K_2C_2O_4\cdot H_2O(s) + H_2O_2(g)$	27.5	25.3	19.9[e]

[a]Data from Ref. [2]. [b]With the assumption that $S^0(\text{salt}\cdot H_2O_2) - S^0(\text{salt}) = 58.2$ J mol^{-1} K^{-1} and using $S^0(H_2O_2) = 232.9$ J mol^{-1} K^{-1} [5]. [c]With the assumption that $S^0(\text{salt}\cdot H_2O) - S^0(\text{salt}) = 39.3$ J mol^{-1} K^{-1} [6] and using $S^0(H_2O) = 188.7$ J mol^{-1} K^{-1} [5]. [d]Assuming ΔH is independent of temperature. [e]$\Delta G_{298} = -RT \ln Kp = -RT \ln P_{H_2O_2}/P_{H_2O}$.

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 H_2O_2 and H_2O vapour pressure [3]. In control experiments, identical samples were exposed to atmospheres of similar humidity controlled by saturated salt solutions. Two perhydrates were examined: $Na_2C_2O_4 \cdot H_2O_2$ which decomposes to the anhydrous oxalate and $K_2C_2O_4 \cdot H_2O_2$ 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 H_2O_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:

Sodium oxalate $Na_2C_2O_4 \cdot H_2O_2(s) \rightleftharpoons Na_2C_2O_4(s) + H_2O_2(g)$

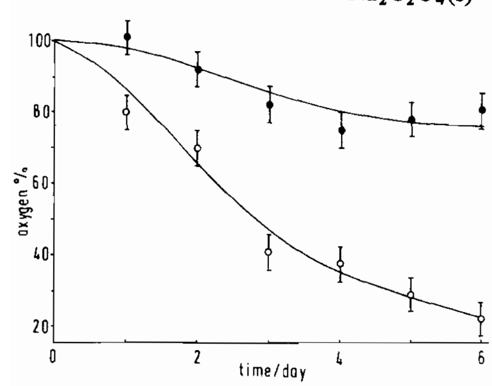

Fig. 2. Decomposition curve for $Na_2C_2O_4 \cdot H_2O_2$ as a function of time at 20 °C. Open circles at 35% RH, filled circles at 35% RH and 0.52 mm Hg H_2O_2 vapour pressure.

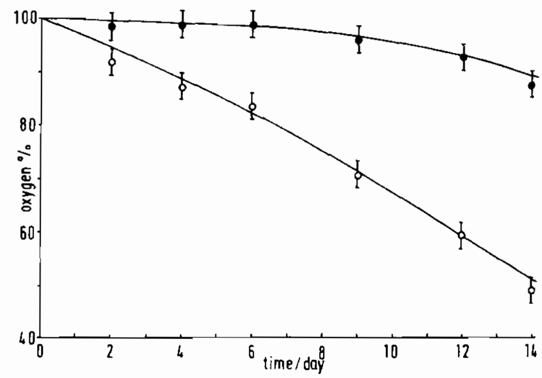

Fig. 3. Decomposition curve for $K_2C_2O_4 \cdot H_2O_2$ as a function of time at 20 °C. Open circles at 88% RH, filled circles at 88% RH and 0.05 mm Hg H_2O_2 vapour pressure.

potassium oxalate $K_2C_2O_4 \cdot H_2O_2(s) + H_2O \rightleftharpoons K_2C_2O_4 \cdot H_2O(s) + H_2O_2(g)$.

Equilibrium constants for these reactions could, in principle, be determined by measuring the pressures of H_2O_2 and H_2O 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 3.2×10^{-4}. Hence the pressure of H_2O_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

1 J. M. Adams, R. G. Pritchard, V. Ramdas and C. J. Adams, *J. Inorg. Nucl. Chem.*, in press.
2 J. M. Adams, G. G. T. Guarini, V. Ramdas and C. J. Adams, *J. Chem. Soc. Dalton*, in press.
3 W. C. Schumb, C. N. Satterfield and R. L. Wentworth, 'Hydrogen Peroxide', ACS Monograph No. 128, Reinhold, New York (1955).
4 'Handbook of Chemistry and Physics', Ed. R. C. Weast, 58th Ed., CRC Press, Cleveland (1977).
5 'JANAF Thermochemical Tables', 2nd Ed., NBS, Washington (1971).
6 W. M. Latimer, 'The Oxidation States of the Elements and their Potentials in Aqueous Solution', 2nd Ed., Prentice Hall, New York (1952).