195. *Thermal Decomposition of Mercuric Oxide.*

By Duncan Taylor.

The kinetics of the thermal decomposition of the orthorhombic form of mercuric oxide have been investigated near 400°. The results are interpreted on the assumption that decomposition occurs only on the surfaces of the particles, leading to a contracting-envelope type of kinetics. The activation energy for the linear progression of the reaction surface has been determined to allow the pre-exponential term in the Polanyi–Wigner rate equation to be calculated. It is concluded that decomposition of the chain structure of the oxide occurs, one molecule at a time, without significant un-zipping action or the triggering-off of mosaic blocks of molecules.

Taylor and Hulett,[1] and Kendall and Fuchs [2] have reported on the rate of the thermal decomposition of mercuric oxide, but without detailed kinetics. Roginsky and his co-workers [3] reported that the decomposition at ~400° followed a contracting-sphere kinetic law [4] if metallic-oxide catalysts were present, but that considerable departure from this law occurred in the absence of catalysts. On the other hand, Erofeev and Trusova [5] found that the decomposition was autocatalysed by the mercury liberated, and, while different samples varied markedly in reactivity, the activation energy was ~57 kcal./mole. The decomposition of the crystalline orthorhombic form in the absence of catalysts has been re-examined in an attempt to establish the kinetics and activation energy and also for the following reasons. Since the decomposition at ~400° is chemically simple (no mercurous oxide exists) and both of the products are gaseous, the kinetics would be expected to follow some type of contracting-envelope process with an activation energy equal to the heat of dissociation [1] (38·2 kcal./mole), provided that decomposition occurs only at the external surfaces, and that nucleation and catalytic effects due to adsorbed mercury or oxygen are not of major importance. Furthermore, as has been found in the dehydration of some salt hydrates and in the decomposition of some carbonates (ref. 4, p. 220, and ref. 6), the rate of decomposition can be expected to agree with the

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[1] Taylor and Hulett, *J. Phys. Chem.*, 1913, **17**, 565.
[2] Kendall and Fuchs, *J. Amer. Chem. Soc.*, 1921, **43**, 2017.
[3] Roginsky, *Ukrain. Chem. J.*, 1929, **4**, 99; *Trans. Faraday Soc.*, 1938, **34**, 961.
[4] For review of kinetic equations see Garner, "Chemistry of the Solid State," Butterworths, London, 1955, p. 184.
[5] Erofeev and Trusova, *J. Phys. Chem. U.S.S.R.*, 1938, **12**, 346.
[6] Britton, Gregg, and Winsor, *Trans. Faraday Soc.*, 1952, **48**, 63.

Polanyi–Wigner equation,[6] *viz.*, rate (molecules cm.$^{-2}$ sec.$^{-1}$) $= N\nu \exp(-E/\boldsymbol{R}T)$, where $N =$ number of molecules per cm.^{2} of reaction interface, and $\nu =$ lattice vibration frequency, $\sim 10^{13}$ sec.$^{-1}$.

EXPERIMENTAL

Preparation of Crystals.—Sample C. Equal volumes of 0·1M-dipotassium tetraiodomercurate and 8N-sodium hydroxide were mixed at room temperature, and the mixture heated slowly to boiling with constant agitation and boiled for 3 min. The precipitate was washed by decantation with cold water, filtered, and dried in air. The product was bright red, well formed prismatic crystals, ~0·02 mm. in size, with some roughly spherical aggregates. *Sample* D. The above procedure, but without agitation and with heating during 1 hr. to 90° followed by 22 hr. at 90°, gave dull red crystals, ~0·1 mm. in size, with many aggregates showing dendritic growths. A very small amount of a pale yellow flocculent precipitate was also formed but was washed from the crystals by decantation with water. For some experiments, a quantity of sample *D* was ground to a fine powder in an agate mortar. *Sample* E. 1% Mercuric chloride (100 c.c.) and 0·1N-sodium hydroxide (75 c.c.) (free from carbon dioxide) were mixed rapidly, both solutions being almost boiling. The precipitate was filtered off, washed with cold water, and dried in air. The product was in the form of very small orange aggregates of very small particles.

X-*Ray Powder Photographs.*—All the samples of crystals gave identical *X*-ray powder photographs, the calculated lattice spacings being the same as those given by Aurivillius [7] for the orthorhombic form.

Kinetic Measurements.—The apparatus (with the addition of a liquid-nitrogen trap near the outlet from the hot reaction vessel) and experimental procedures were similar to those already reported.[8] Samples of oxide (9—22 mg.) were decomposed in an open platinum bucket at 379—457°, the volume of the reaction system being such that the final oxygen pressures did not exceed 0·1 mm. The reaction was followed by measuring the oxygen pressure with either a Macleod gauge (sample *E*) or a recording Pirani gauge (samples *C* and *D*). The latter was kept at 25° (thermostat), calibrated with oxygen against the Macleod gauge, and protected from mercury vapour by liquid-nitrogen traps. The Pirani gauge deflection varied linearly with oxygen pressure up to 0·1 mm. Under these conditions, recombination of the mercury and oxygen formed was insignificant since the final oxygen pressure was within a few percent of theory, and, after several runs, only a very slight yellow film of oxide appeared on the cold walls of the system immediately above the hot reaction vessel. Experiments with a capillary-leak system connected to the apparatus in place of the reaction vessel showed that, over the range of decomposition rates measured, delays due to slow diffusion of oxygen from the reaction vessel to the rest of the system were not significant. Storage of samples *C* and *D* for 2 years in air in the dark had no effect on the kinetics; the heating of sample *D in vacuo* for 19 hr. at 331° caused 0·006% decomposition and changed the colour from dull to bright red, but did not alter the kinetics of subsequent thermal decomposition at 411—457°.

RESULTS AND DISCUSSION

The results can best be interpreted in terms of a contracting-envelope process having a substantially constant rate in the early stages.[9] Thus, a prominent feature of the pressure–time curves was the virtually linear rate at all temperatures over the range 10—40% decomposition for samples *C* and *D* (whole crystals) and 5—20% for sample *E* (Fig. 1). In many of the experiments the same linear rate was observed right from the start of the decomposition, but in some at the lower temperatures very slight acceleration occurred before the constant rate was established. Such acceleration is attributed not to heating effects (heating after the lowering of samples into the hot reaction vessel took less than 5 minutes), but to slight increase in the effective surface of the particles due to roughening and to break-up of crystal aggregates in the first few percent of the decomposition. Since the slight acceleration was observed in only a minority of the

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[7] Aurivillius, *Acta Chem. Scand.*, 1956, **10**, 852.
[8] Taylor, *J.*, 1955, 1033; 1958, 2378, 3323.
[9] Cf. Jacobs and Tompkins, *Proc. Roy. Soc.*, 1953, *A*, **215**, 273.

experiments autocatalysis by mercury vapour as reported by Erofeev[5] is an unlikely explanation. At the higher temperatures with sample *D* (whole crystals) an initial rapid evolution of gas, equivalent to 2—3% decomposition, occurred before the linear rate, and may have been due to rapid decomposition either at active sites or of very small particles. The activation energies (kcal./mole) calculated by the method of least squares from the temperature coefficients of the linear rates were: *C*, 44·5 ± 2·2; *D* (whole crystals), 48·1 ± 1·4; *E*, 38·8 ± 1·9, where the probable errors are standard deviations. The decrease in activation energy with decreasing crystal size is just significant. For sample *D*, after being ground, the maximum rate occurred within 2 minutes of the start of the decomposition, the rate decreasing continuously thereafter. The results were well represented by the contracting-sphere equation, $kt = 1 - (1 - \alpha)^{1/3}$, where α is the fraction decomposed at time t over the range 0—70% decomposition (Fig. 2). The temperature coefficient of k gave an activation energy of 44·9 ± 1·7 kcal./mole.

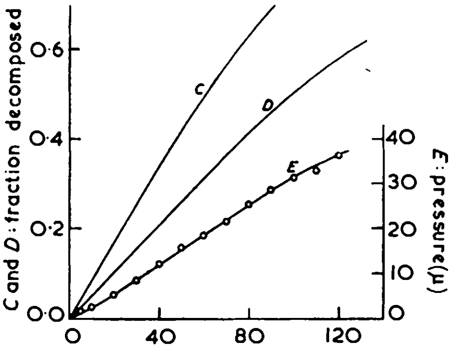

FIG. 1. Transcribed recorder traces for samples *C* and *D* (whole crystals), and oxygen pressure–time curve for sample *E*. Decomposition temperatures: *C*, 409·4°; *D*, 427·4°; *E*, 383·8°.

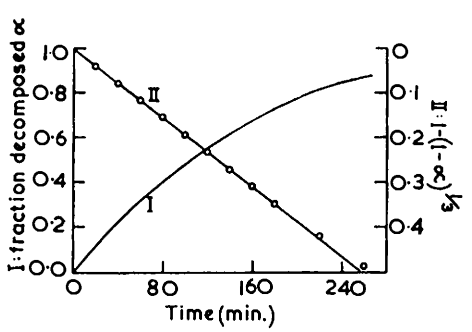

FIG. 2. Transcribed recorder trace (curve I) and plot of contracting-sphere law equation (curve II) for sample *D* after grinding. Decomposition temperature 413·4°.

It must be emphasised that, in spite of the apparently linear rates, the results for all samples (except *E* where measurements were not continued beyond the end of the apparently linear stage) fitted the contracting-sphere equation very well over the major part of the decomposition, but that the equations for contracting circular or rectangular plates[4] (*i.e.*, corresponding to two-dimensional contracting envelope processes) were often equally satisfactory, as was also the first-order decay equation in a minority of the experiments and the Avrami equation for sample *D* (whole crystals). It is considered, however, that the results as a whole are most consistent with a contracting-envelope mechanism, although the decision between a two- and a three-dimensional process could not be made with certainty. It is nevertheless possible, in view of the remarkable linearity of the recorder traces in the 10—30% decomposition range for samples *C* and *D* (whole crystals), that in the early stages the process was in fact one-dimensional and proceeded in only one crystallographic direction (cf. late stages in the decomposition of ammonium dichromate[8] and lead styphnate[10]). The fact remains however that the quoted activation energies correspond to the linear progression of the reaction surface through the crystals.

Aurivillius[7] has reported that the orthorhombic form of mercuric oxide consists of planar zig-zag chains of alternate mercury and oxygen atoms running parallel to the *a*-axis and lying in the *ac*-plane. He suggests that the chains are mainly homopolar, with weak forces between adjacent chains. Taylor and Hulett[1] have shown that the

[10] Flanagan, *Trans. Faraday Soc.*, 1961, **57**, 797.

heat of dissociation corresponding to the reaction $HgO(s) \longrightarrow Hg(v) + \frac{1}{2}O_2(v)$ is 38·2 kcal./mole. It appears therefore, since the activation energies (between 38·8 and 48·1 kcal./mole) are decidedly less than twice the heat of dissociation, that in the transition state of the decomposition only one molecule of oxide is involved and that the chains decompose one molecule at a time. This mechanism for well-crystallised material could lead ideally to a one-dimensional process, at least in the early stages. If 38 kcal./mole is taken as the true activation energy for the linear progression of the reaction surface, it may be that, for samples *C* and *D*, ~7—10 kcal./mole are required for what may be termed a nucleation process and one which would have to proceed continuously throughout the decomposition owing to the evaporation of the products. The very finely divided material *E* would not appear to require such nucleation.

On the assumption that sample *D* (whole crystals) consists of spherical particles, diameter 0·1 mm., the corresponding surface area together with the linear rate and appropriate activation energy, gave a value of ν, calculated from the Polanyi–Wigner equation, of 10^{15} sec.$^{-1}$. The surface areas of the other samples are less certain, but reasonable areas gave values of ν between 10^{11} and 10^{15} sec.$^{-1}$. Probable errors in the estimated areas and in the activation energies led to an uncertainty of, at the most, three orders of magnitude in the value of ν. The frequency factor in the rate equation is therefore barely large enough to be considered abnormally high for a solid-state reaction. Values of the order 10^{18} sec.$^{-1}$ and greater, observed for the dehydration of chrome alum (ref. 4, p. 220) and for polymorphic transformations of sulphur [11] and of azoxybenzene,[12] belong unambiguously to the high range of values and have been explained on the basis that a single act of excitation and decomposition triggers off the decomposition of the whole of a mosaic block of molecules. Such a process, or the un-zipping of long –Hg–O– chains, evidently does not occur with orthorhombic mercuric oxide.

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[11] Hartshorne, *J.*, 1935, 1860; 1938, 310; 1940, 588; 1951, 1097.
[12] Hodkin and Taylor, *J.*, 1955, 489.