494. *The Kinetics of the Decomposition of Stannane on a Tin Surface.*

By S. F. A. Kettle.

The kinetics of the decomposition of stannane between +50° and −50° have been studied in a static system. The rate is of first order in stannane above −10°, but kinetic anomalies appear below this temperature. These anomalies may be related to the appearance of the grey modification of tin on the catalytic surface. Oxygen acts as a catalyst at low partial pressures but at higher pressures inhibits the decomposition of stannane.

Although it is well known that stannane decomposes autocatalytically,[1] the only kinetic investigation was carried out by Tamarau.[2] He studied the decomposition on a tin surface in the range 35—100° and found the rate to be of the first order with respect to stannane, hydrogen not being adsorbed.[3]

The present work was carried out at lower temperatures, since below 13° grey tin is the stable allotrope[4] and its presence on the catalytic surface would presumably change the kinetics of the decomposition. Kinetic anomalies have indeed been found and may be explained largely, if not completely, by the presence of grey tin.

Tamarau found that oxygen prevented the decomposition of stannane and so worked with a pressure of less than 10^{-5} mm. in his apparatus. A further investigation of this effect shows that at very low pressures oxygen exhibits a catalytic effect.

The kinetics observed in the temperature range −10° to +50° were in reasonable agreement with those reported by Tamarau.[2] Plots of log (stannane pressure) against time were excellent straight lines, confirming that the decomposition is of the first order in stannane and unaffected by adsorption of hydrogen. The apparent activation energy was $10{\cdot}9 \pm 0{\cdot}3$ kcal. mole^{-1}, this being the average from three sets of runs. The results from two of these sets are shown in Figs. 1 and 2. A value of 9·1 kcal. mole^{-1} for the apparent activation energy was reported previously.[2]

At temperatures below −10° the catalytic surface was found to " age " quite rapidly. If the reaction vessel was kept at such a temperature for more than about six hours stannane did not decompose when admitted. Cooling to −50° for one hour caused the catalytic tin surface to fragment and fall to the bottom of the decomposition vessel. Subsequent *X*-ray analysis showed that although the fragments were largely

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[1] Paneth, Haken, and Rabinowitsch, *Ber.*, 1924, **57**, 1891; Finholt, Bond, Wilzbach, and Schlesinger *J. Amer. Chem. Soc.*, 1947, **69**, 2692.

[2] Tamarau, *J. Phys. Chem.*, 1956, **60**, 610.

[3] Trapnell, *Proc. Roy. Soc.*, 1953, *A*, **218**, 566.

[4] Cohen and Van Lieshout, *Z. phys. Chem.*, 1935, **173**, 32.

white tin, they also contained some of the grey allotrope. The relative proportions are not significant since grey tin rapidly reverts to the white modification at room temperature.

A further indication of the "ageing" of the surface was shown by the non-reproducibility of kinetic results obtained below —10°. Two successive runs at the same temperature and initial pressure invariably gave different results. The disparity between the runs increased with the time interval between them.

Fig. 1 shows the results obtained from a series of runs in which the temperature was cycled. From *ca.* +50° to —10° the rate is of the first order in stannane, but from —10° to —30° it is almost constant, showing a slight negative temperature coefficient. The rate then rapidly decreases until, at —44°, it becomes zero. Raising the temperature in *ca.* 30° steps did not initiate decomposition until 40°, where, after an induction period decomposition recommenced, the rate increasing until it was approximately that obtained earlier at about the same temperature. Further runs on the reactivated surface gave a plot of log *k* against T^{-1} parallel to that obtained before deactivation.

FIG. 1. *An Arrhenius plot of runs for which the temperature was "cycled," i.e., first reduced, then increased, and finally decreased again.*

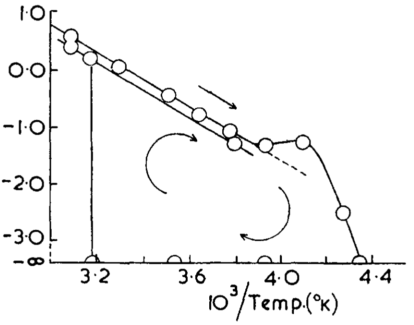

FIG. 2. *An Arrhenius plot which shows the ageing of a catalytic tin surface at ca. —10°.*

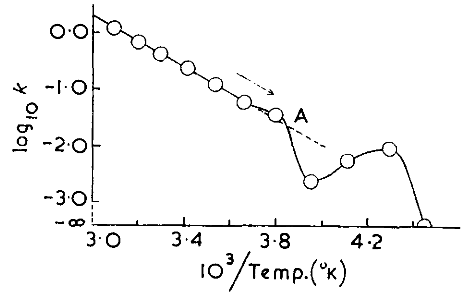

FIG. 3. *The effect of oxygen on the rate of decomposition of stannane.*

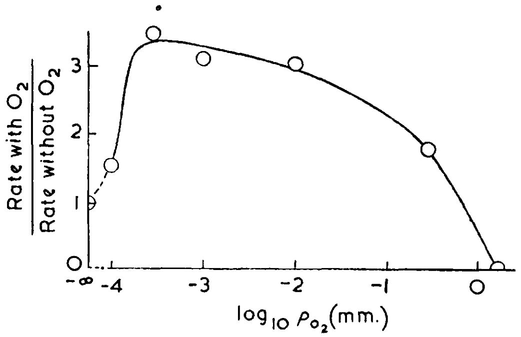

FIG. 4. *The decomposition of stannane at 20° in the presence of 1 mm. of oxygen.*

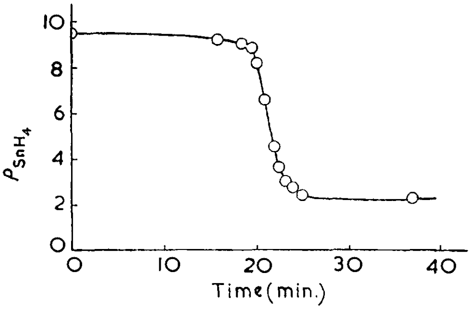

Fig. 2 provides a good example of the effect of the " ageing " of the catalytic surface at —10°. The decomposition vessel was held at point A (—10°) for two hours before the series of runs was continued. During the interruption the surface became a less active catalyst, but the newly deposited tin coating restored much of the activity, producing a rate with an apparent negative temperature coefficient.

It is evident that, because of the time-dependance of the reaction rates, Arrhenius plots obtained at low temperatures depend on the particular experimental procedure followed. Figs. 1 and 2 are two particular procedures chosen from many possible alternatives.

The most obvious explanation of the phenomena observed at low temperatures is that grey tin is catalytically inactive and that a surface changing from white to grey tin is more effective than white tin alone. There is, however, only indirect evidence of the amount of grey tin present. It may well be that only a very small extent of allotropic conversion is required to poison a catalytic white-tin surface completely. It was not found possible to decompose stannane at temperatures below —40°; it is reported[5] that the white ⟶ grey transformation is fastest at —48°.

Other effects may also be involved: (1) Cooling a thin tin film may cause surface strains or surface disruptions. Either might be expected to produce deviations from a simple kinetic behaviour. The fragmentation of a catalytic tin surface at —50° strongly suggests that these may be important factors. (2) It is a general phenomenon that at high pressures and/or low temperatures first-order rates for heterogeneous reactions with non-adsorbed products should become fractional and finally of zero order. This is associated with the increased adsorption of the reactants on to the catalytic surface. Such an effect may be occurring in the present research, but there is no evidence on the point.

The effect of added oxygen on the rate of decomposition of stannane at 20° is shown in Fig. 3. At a partial pressure of about 5×10^{-4} mm., oxygen shows its maximum catalytic effect, increasing the rate by a factor of 3—4. If we assume the tin surface to be perfectly smooth, at this pressure the ratio (surface tin atoms) : (oxygen atoms) is about 100 : 1. The catalytic effect of oxygen decreases as its partial pressure is further increased, until at 1 mm. it completely stops the decomposition of stannane. This observation finds application on the preparation of stannane, when, by having oxygen in the carrier-gas stream, the yield is increased. Presumably the autocatalytic decomposition of the product is inhibited.[6] It is also possible to store stannane at room temperature if it is mixed with oxygen.[6]

In those runs for which first-order kinetics were not obeyed initial rates were taken and are those plotted in Figs. 1—3. For Fig. 3 this procedure is not entirely satisfactory. Although Fig. 3 indicates that 1 mm. of oxygen "completely stops the decomposition of stannane," Fig. 4, which shows in detail the effect of 1 mm. of oxygen on a typical run at 20°, shows that the initial rate of zero corresponds to an induction period of about 15 min. After this induction period decomposition is very rapid but then virtually stops when about 20% of the stannane remains. Some features of the results obtained in the presence of oxygen appear to be almost independent of temperature and of oxygen concentration. An example is the cessation of decomposition when *ca.* 20% of the initial stannane remains. However, since these results are only roughly reproducible, no conclusions can safely be drawn.

EXPERIMENTAL

Stannane was made by the reduction of stannic chloride with lithium aluminium hydride in ether.[6] Stannane prepared by this method has been shown to give the purest tin yet obtained [7] (impurities $\ngtr 0{\cdot}00004\%$).

The kinetic apparatus, shown in Fig. 5, was made of Pyrex glass. After thorough evacuation and flaming, the decomposition vessel D was plated with tin by admitting stannane to a pressure of 10 cm. and initiating its decomposition with a flame. Further portions of stannane were then decomposed; when the tin surface was opaque it gave reproducible kinetic results. The decomposition was followed by the pressure change, indicated by the spiral gauge S. This gauge was sensitive to pressure changes of 0·1 mm. and its calibration (deflection *versus* pressure difference) was reproducible to ±2 mm. The dead volume of the kinetic apparatus was 1·1% of the total. A vacuum of less than 10^{-5} mm. in the wide-bore part of the apparatus was

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[5] Cohen and Von Eijk, *Z. phys. Chem.*, 1899, **30**, 601.

[6] Emeléus and Kettle, *J.*, 1958, **2444**.

[7] Brenner, Bierig, and Marsel, 17th Internat. Congr. Pure Appl. Chem., Münich, 1959, Paper A 226; also personal communication from W. Brenner.

obtained by using two mercury pumps in series, backed by a rotary pump. The decomposition vessel was surrounded with a 5-l. Dewar flask containing water or acetone. The bath-liquid was stirred throughout all of the runs since the spiral gauge was unaffected by the slight vibration. An acetone-expansion thermoregulator controlled an electrical heater: for low-temperature runs the bath-liquid was cooled with a cold finger filled with solid carbon dioxide. The cold finger was lowered into the bath-liquid to a depth which caused the latter to cool slowly; the electrical heater, controlled by the thermoregulator, then maintained the temperature. The bath-temperature was constant to ±0·1°.

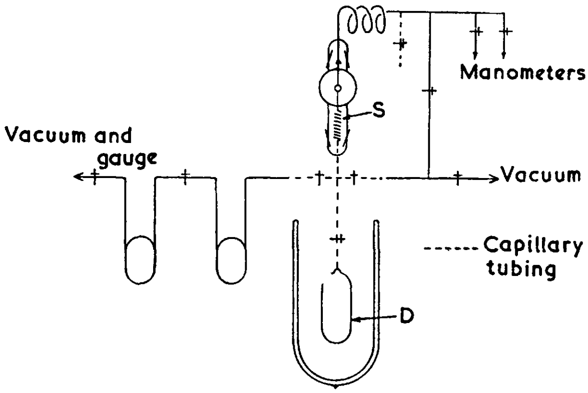

FIG. 5. *The kinetic apparatus.*

The oxygen used in the study of its effect on the decomposition of stannane was prepared by heating potassium permanganate in an evacuated flask, and was passed through a trap at −196°. Oxygen pressures were measured with a McLeod gauge; for very low pressures only the dead volume in the decomposition vessel was filled. When this oxygen was admitted to the decomposition vessel its pressure was reduced by a factor of 91. At the end of a run the decomposition vessel was evacuated to as low a pressure as possible. To reduce the effect of retained oxygen the next run was carried out with the oxygen pressure increased ten-fold.

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