

ment for the phosphides of gallium and indium, which are stable in the presence of non-oxidizing acids.

The X-ray photographs of the products obtained, after purification, contain no lines due to impurities or to phosphides of different composition. Unreacted metals (Al, Ga, In), if present in the end products, are therefore in trace amount concentration. While in preparations on a laboratory scale the zinc obtained in the reactions is not worth saving, a continuous process can be envisaged, in which the zinc is retransformed into zinc phosphide and this reacts again with the third group elements. This possibility makes the process interesting from the standpoint of the

industrial production of the phosphides of aluminum, gallium and indium.

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The Thermal Decomposition of Silver Oxide

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The results of the thermal decomposition of silver oxide, freed from silver carbonate by preheating at 280° for 3 hr. *in vacuo*, are highly reproducible. Study of the kinetics of the reaction in the range 330–380° has shown that the pressure-time curves over the acceleratory region are represented by the equation $P^{1/2} = kt + c$. Reaction proceeds by the growth of two-dimensional nuclei with an activation energy of 28.3 kcal./mole. The decay stage follows a unimolecular law and the activation energy is 29.6 kcal./mole. Pre-irradiation by ultraviolet light, cathode rays, ⁶⁰Co γ-rays, thermal neutrons and fast neutrons has no effect on the subsequent thermal decomposition.

The thermal decomposition of silver oxide has been investigated by various workers. Their results show discrepancies between the activation energies, the form of the pressure-time curves and the mathematical relationships describing such plots.

Lewis¹ prepared silver oxide from silver nitrate and barium hydroxide (or sodium carbonate). The oxide was heated in oxygen at atmospheric pressure at 320–350°. The decomposition, in the case of the first specimen (Merck silver oxide), was preceded by very long induction periods. None of the prepared specimens showed this property. In all cases the equation

$$dx/dt = kx(1 - x) \quad (1)$$

where x is the fractional number of moles of silver oxide decomposed, was obeyed. The activation energy for the reaction was 31.8 kcal./mole.

Hood and Murphy,² using a similar procedure, confirmed the results of Lewis. The integrated form of equation 1

$$\ln x/(1 - x) = kt + c \quad (2)$$

was applicable.

Pavlyuchenko and Gurevich³ prepared silver oxide in darkness, and in the presence of air, by adding an aqueous solution of KOH to an aqueous solution of AgNO₃ at 5°. They obtained complex pressure-time curves and a low activation energy of 10.2 kcal./mole. Decomposition was carried out *in vacuo* in the relatively low temperature range of 118–220°.

(1) G. N. Lewis, *Z. physik. Chem.*, **52**, 310 (1905).

(2) G. C. Hood and G. W. Murphy, *J. Chem. Educ.*, **26**, 169 (1949).

(3) M. M. Pavlyuchenko and E. Gurevich, *J. Gen. Chem., U.S.S.R. (Eng. Transl.)*, **21**, 511 (1951).

Benton and Drake⁴ decomposed silver oxide prepared by the combination of silver and oxygen. The decomposition temperature was 150° lower than that of Lewis and the activation energy was 35–36 kcal./mole.

Averbukh and Chufarov⁵ decomposed silver oxide on a spring balance. The rate of decomposition for a constant degree of dissociation was determined and an activation energy of 29.0 kcal./mole was calculated.

Garner and Reeves⁶ repeated the preparations of Lewis and decomposed the oxide at 300–330° in vacuum. The pressure-time plots showed no induction period but gave a maximum rate at the beginning of the reaction. The curves were irregular and not of an autocatalytic type. As well, specimens of silver oxide were annealed in oxygen at 28–38 atm. for 8–10 days at 200–300° to yield a dense coarsely crystalline oxide which decomposed *in vacuo* to yield sigmoid curves for the pressure-time plots. The autocatalytic relation of Lewis was not valid, but it was considered that the plots were described by the power law

$$P^{1/2} = kt + c_1 \quad (3)$$

It was not possible to determine the activation energy in the usual manner due, presumably, to the irreproducibility of results from sample to sample. Instead split runs on the same specimen of oxide at different temperatures were performed. The activation energy for the reaction was 45.6–46.2 kcal./mole.

(4) A. F. Benton and L. C. Drake, *THIS JOURNAL*, **56**, 255 (1934).

(5) B. D. Averbukh and G. I. Chufarov, *Zhur. Fiz. Khim.*, **23**, 37 (1949).

(6) W. E. Garner and L. W. Reeves, *Trans. Faraday Soc.*, **50**, 254 (1954).

The reported effects of light on the decomposition differ.^{3,6}

The mathematical relationships applied by Lewis, Hood and Murphy, and Garner and Reeves, did not in any instance describe the complete decomposition curve. In none of the above preparations of silver oxide was it reported that stringent precautions were taken to exclude atmospheric carbon dioxide from the oxide immediately prior to decomposition. In view of the reactivity of silver oxide with carbon dioxide⁷ it was considered that the differing results might be explained by the contamination of the oxide by silver carbonate prior to decomposition. Consequently, the decomposition was re-investigated.

The thermal decompositions of KMnO_4 ⁸ and AgMnO_4 ⁹ are accelerated by pre-irradiation of the solids in BEPO and in a ⁶⁰Co hot-spot. A theory based on the annealing of point defects with the formation of decomposition spikes has been proposed. It was of interest to extend the study of the effects of irradiation to Ag_2O .

Experimental and Results

Apparatus.—The apparatus consisted of a pumping system, a McLeod gauge with a pressure range of 10^{-1} to 10^{-3} cm. and a constant temperature decomposition vessel. The latter consisted of a Pyrex tube of 1.5 cm. diameter (the decomposition tube) closed at one end and internally sealed into a Pyrex tube of 6 cm. diameter (the furnace tube) so that the closed end was situated in the center of the larger tube. The other end of the furnace tube was sealed to a thick-wall Pyrex tube of 2 mm. diameter. A 100 watt heater was wound onto the furnace tube. Expansion and contraction of the air in the annular space of this apparatus altered the pressure on a column of mercury in the 2 mm. tubing which in turn operated a conventional mercury thermostat control and relay connected to the heater. The furnace was placed in an asbestos box and surrounded by vermiculite. This box and the regulator system were placed in a larger box containing no packing. A winch system was used to lower the platinum (or silica) decomposition bucket into the decomposition tube. A calibrated mercury thermometer was placed in the tube. The temperature control in the range 300–380° was $\pm 0.1^\circ$ over long periods.

Materials.—The barium hydroxide (twice recrystallized in the absence of CO_2) and the silver nitrate were "AnalaR" chemicals. Several specimens of silver oxide were used and all preparations were done under dark-room conditions.

A. Merck's "Pro-Analysis" silver oxide. The bottle had been opened some months previously.

B. A specimen made by a method similar to Garner and Reeves preparation B and Lewis' second and third preparations. A saturated aqueous solution of $\text{Ba}(\text{OH})_2$ was added, dropwise, to a saturated aqueous solution of silver nitrate at room temperature until precipitation was complete. The precipitate was dried *in vacuo* over silica gel.

C. This specimen was prepared under conditions in which the contamination of all solutions, water and solids by atmospheric carbon dioxide was reduced to a minimum. Conductance water (conductance at 25°, 80 nanomho/cm.) was used. The apparatus was similar to that of Riley and Baker.⁷ The silver oxide was dried *in vacuo* at room temperature for four days before use. The oxide was stored and weighed as far as possible in an atmosphere of nitrogen.

D. Silver carbonate was prepared from 0.1 N AgNO_3 and 0.1 N Na_2CO_3 at $\pm 5^\circ$ and dried *in vacuo* over silica gel for three days. The carbonate was decomposed in a platinum bucket in the high vacuum line for 3 hr. at 200° with continuous pumping. The bucket was raised from the decomposition chamber, the furnace temperature increased to 350° and the decomposition of the silver oxide commenced.

Specimen A was black in color. Specimens B and C, and the silver oxide obtained from Specimen D, were chocolate

brown in color. Riley and Baker⁷ have stated that pure silver oxide is brown and not purple-black as usually observed.

The Thermal Decomposition of the Above Specimens.—In all cases ~ 20 mg. of the oxide was decomposed at 350°. All the specimens gave irreproducible results although for a particular preparation the shapes of the pressure-time plots were similar. The types of curves are shown in Fig. 1. Normalization to a common pressure was done in all cases.

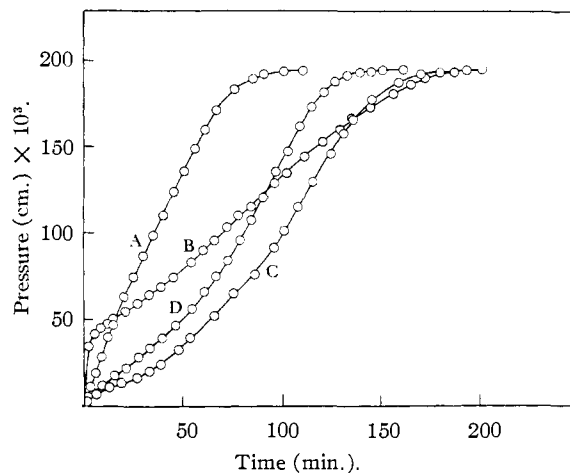


Fig. 1.—Pressure-time plots for decomposition of specimens A, B, C and D at 350° with no KOH or pre-heating.

No further work was done with Specimen A. The insertion of a P_2O_5 trap between the decomposition chamber and the pressure gauge did not improve the reproducibility or alter the general shapes of the curves. Replacement of the P_2O_5 trap by one containing KOH pellets altered all the pressure-time plots. In the case of Specimen C the small initial fast reaction was eliminated but the general shape of the curve was retained. It seemed that, despite precautions, very slight contamination of specimen C by carbon dioxide had occurred. The pressure-time plots of all other specimens were reduced to this form. However, reproducibility was still not satisfactory. Since a study of pre-irradiation effects could be made only with silver oxide free from carbonate, attempts were made to remove the small amount of carbonate by heating specimen C. In the following account, unless specifically stated, the oxide used was Specimen C. Samples of the oxide were heated at various temperatures and for different periods of time in the high vacuum apparatus.

TABLE I

PRESSURE-TIME DATA FOR DECOMPOSITION AT 350° OF 20 MG. OF OXIDE PREHEATED AT 280° FOR 3 HR.

<i>t</i> (min.)	<i>P</i> × 10 ³ cm.	<i>t</i> (min.)	<i>P</i> × 10 ³ cm.
0.5	0.035	87	81.25
3	0.23	93.5	91.19
6	1.45	99	99.90
9	3.51	105	110.1
12	5.55	111	122.0
15	7.81	118	135.6
21	11.47	123	145.5
27	16.38	129	157.1
33	20.49	135	167.6
39	25.21	141	176.0
45	31.36	147	182.4
51	36.30	153	186.2
57.5	43.27	159	190.5
63	48.21	166.5	193.4
69	56.05	171	194.8
75	62.73	177	196.3
81	71.15	186	196.6
84	74.63	195	197.5

P_f 197.6

(7) H. L. Riley and H. B. Baker, *J. Chem. Soc.*, 2510 (1926).

(8) E. G. Prout, *J. Inorg. & Nuclear Chem.*, **7**, 368 (1958).

(9) E. G. Prout and M. J. Sole, *ibid.*, **9**, 232 (1959).

Pre-heating at 280° for 3 hr. produced specimens which decomposed at 350° to yield pressure-time plots which were singularly reproducible. There was no change in color after pre-heating. Four consecutive runs gave pressure-time plots which were almost superimposable. Typical pressure-time data are given in Table I. Decomposition of pre-heated specimens in the presence, or absence, of the KOH trap yielded identical pressure-time plots, thus indicating that the silver oxide was free of carbonate after pretreatment. Analysis of the gas liberated during the preheating of 300 mg. of the oxide showed the presence of CO₂ and no O₂. Thus, no measurable decomposition of the oxide occurred during pre-treatment. This was confirmed by the chemical analysis of the preheated oxide. The oxide was weighed in an atmosphere of nitrogen, dissolved in 0.2 *N* nitric acid and the silver estimated by Volhard's method. This gave a purity of the silver oxide of 99.94%. Contamination of the silver oxide was demonstrated by exposing pre-heated specimens to air and CO₂ for various lengths of time. The results are shown in Fig. 2.

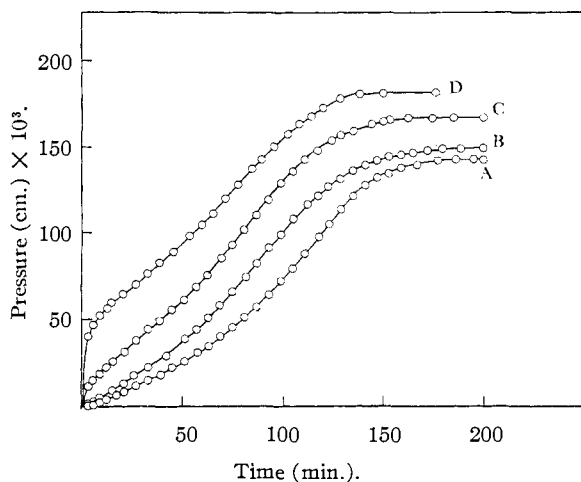


Fig. 2.—Pressure-time plots showing effects of exposing pre-heated oxide to air at room temperature for, A = 0 min., B = 10 min., C = 13 hr. For curve D the oxide was exposed to CO₂ for 18 hr.

Grinding the pre-heated oxide in an agate mortar and in an atmosphere of nitrogen had no effect. Similarly, interruption of the decomposition at various stages did not alter the kinetics of the reaction. No effect was found when the platinum bucket was substituted by a quartz one.

Effect of Ultraviolet Light and Cathode Rays.—Specimens of silver oxide were pre-heated at 280° in silica tubes which then were filled with nitrogen and sealed. Exposure to a full quartz/mercury arc for 4.5 hr. at 8 cm. at room temperature had no effect on the subsequent decomposition at 350°. Bombardment of the pre-heated salt with cathode rays (applied potential 20 kv., residual O₂ pressure 2 × 10⁻⁸ cm.) prior to decomposition had no effect.

Effect of End Products.—The decomposition of 20 mg. of pre-heated Ag₂O was unaffected by the prior admixture, in an atmosphere of nitrogen, of the solid residue from a previous decomposition. Oxygen was generated in the apparatus by the decomposition of 20 mg. of pre-heated Ag₂O in a second decomposition chamber. The decomposition of pre-heated Ag₂O at 350° in this atmosphere was not affected. Pre-heating at 280° for 3 hr. in oxygen at one atmosphere did not alter the decomposition at 350°.

Effect of Pre-irradiation.—Specimens of Ag₂O were prepared as for the ultraviolet runs. Pre-irradiation in BEPO in a position near the outside (thermal neutron flux, 2 × 10¹¹ n./cm.²/sec.) for 48 hr., in a hollow uranium slug (fast neutron flux, 3 × 10¹¹ n./cm.²/sec.) for one week, and in a ⁶⁰Co hot-spot (dose rate, 1.6 × 10⁶ r.e.p. hr⁻¹) for 48 hr., produced no effect on the subsequent decomposition at 350°; the pressure-time curves of irradiated and unirradiated specimens were almost superimposable.

Mathematical Analysis of the *P-t* Plots.—The extent of applicability of equation 3 and the Prout-Tompkins

equation¹⁰

$$\log P/(P_t - P) = k_2 t + c_2 \quad (4)$$

was examined. These equations did not represent the curves. The expressions

$$P^{1/2} = k_3 t + c_3 \quad (5)$$

and

$$\log (P_t - P) = k_4 t + c_4 \quad (6)$$

were, however, applicable over the acceleratory and decay periods, respectively (Fig. 3).

The pressure-time curves for the decomposition of pre-heated Specimen D also were represented accurately by equations 5 and 6.

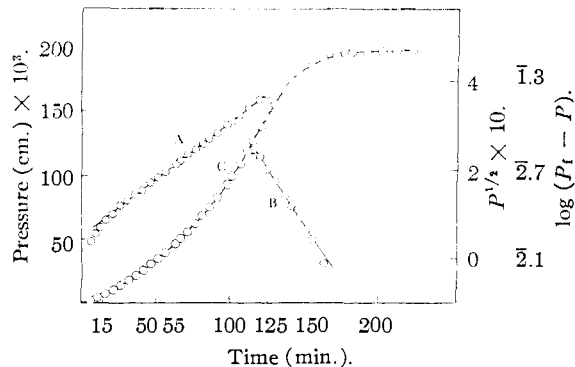


Fig. 3.—Lines A and B: plots for $P^{1/2}$ against t , and $\log (P_t - P)$ against t , respectively; Curve C: pressure-time plots for decomposition at 350°.

Activation Energies.—A series of decompositions was carried out in the range 330–380° on specimens of preparation C pre-heated at 280° for 3 hr. The results were analyzed by applying equations 5 and 6. The plots of $\log k_3$ and $\log k_4$ against $1/T$ (°K.) are shown in Fig. 4. The calculated activation energies were $E_3 = 28.3$ kcal./mole and $E_4 = 29.6$ kcal./mole.

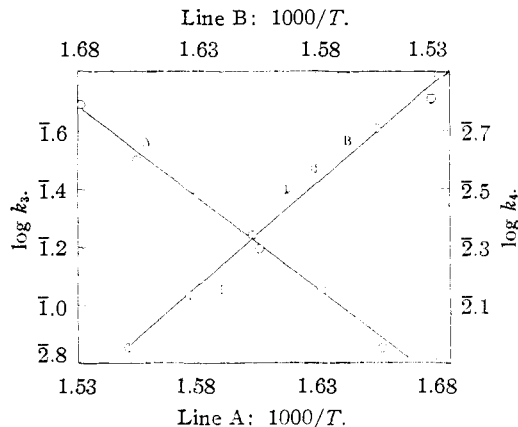


Fig. 4.—Lines A and B: activation energy plots for acceleratory and decay stages, respectively.

Discussion

The decomposition of silver oxide free from silver carbonate is reproducible and yields a normal sigmoid pressure-time curve. The irreproducibility of results found by previous workers apparently was due to reaction of the specimens with atmospheric carbon dioxide during storage and handling. The occurrence of a maximum rate of decomposition at the commencement of the reaction as found by Pavlyuchenko and Gurevich⁵ and Garner and Reeves,⁶ apparently represented the rapid decom-

(10) E. G. Prout and F. C. Tompkins, *Trans. Faraday Soc.*, **40**, 488 (1944).

position of silver carbonate. The elimination by Garner and Reeves of this maximum rate using annealed silver oxide probably was due to the extremely large reduction in surface area of the oxide during the annealing. The larger particles (diameter ~ 0.8 mm.) would have formed much less silver carbonate than the finely divided powder of the original preparation. The diameter of the particles of our preparation B, which was similar to Garner's, was $\sim 4.0 \times 10^{-3}$ mm. The reported sensitivity of silver oxide to light presumably was due to the presence of silver carbonate.

The pressure-time plots of Hood and Murphy, while not covering the complete decomposition, resemble those shown here. Pressure measurements were carried out with a differential water manometer, the evolved CO_2 thus largely dissolving in the water.

The acceleratory stage of the decomposition is fitted by a square-root plot as opposed to the cube-root plot applied by Garner and Reeves.⁶ The square-root relationship indicates two-dimensional growth of a fixed number of nuclei. In a precipitated solid, such as specimen C, the density of dislocations will be high. A number of these, especially after annealing at 280° for 3 hr., would be concentrated in sub-boundaries. During decomposition two-dimensional growth of the nuclei would possibly occur along such boundaries. The negative intercept on the abscissa of the plot of $P^{1/2}$ against t shows that initially the growth of the nuclei is abnormally fast. The discrepancy between our findings and those of Garner and Reeves⁶ might be explained by the following observations. The cube-root plot which they applied does not always appear to be linear. In Fig. 1 of their paper the plot of $P^{1/2}$ against t for the decomposition at 315.7° shows a distinct curvature of the line. The same applies to certain of the "split-run" curves in Fig. 3. A photographic enlargement of the plots for the decomposition at 315.7° was made and a straight line was obtained using the square-root relationship.

The activation energy of 28.3 kcal./mole is in reasonable agreement with the value found by Lewis,¹ Hood and Murphy² and Averbukh and Chufarov.⁵ The estimated accuracy of our result is ± 1.5 kcal./mole.

The acceleratory stage of the decomposition proceeds by a mechanism of non-branching two-dimensional reaction planes and it is to be expected that after interference of the planes the undecomposed silver oxide will consist of isolated blocks of material in which no nuclei are present. In these blocks if each molecule possesses an equal probability for decomposition, then the rate of reaction will be proportional to the amount of substance undecomposed and the unimolecular decay law 6 will apply.

The mechanism suggested for the decomposition of pre-irradiated KMnO_4 and AgMnO_4 involves the annealing of point defects and the accumulation of strain in the crystal over the induction period. The strain results in cracking or fracturing of the solid and reaction occurs in these new reactive surfaces by a branching chain mechanism. The absence of any similar observable effect with pre-irradiated silver oxide may be associated with the fact, as shown by grinding, that the creation of new surfaces does not increase the rate of reaction. As well, it is possible that annealing of the point defects may not occur at the decomposition temperature. Silver oxide is a covalent compound and in such compounds defects appear to be very stable. For example, heating irradiated (fast neutrons) quartz at 100° for three weeks produces no observable recovery of the thermal conductivity change, and heating well above the α - β transition point (573°) is required before any major recovery occurs.¹¹

The authors wish to thank the C.S.I.R. (S.A.) for a grant to cover the cost of irradiations and African Explosives and Chemical Industries for a scholarship held by P.J.H.

(11) R. Berman, P. G. Klemens, F. E. Simon and T. M. Fry, *Nature*, **166**, 864 (1950); R. Berman, *Proc. Roy. Soc. (London)*, **A208**, 90 (1951).

[CONTRIBUTION FROM THE LABORATORY OF CHEMICAL SPECTROSCOPY, TOKYO INSTITUTE OF TECHNOLOGY]

The Molecular Complexes between Iodine and Various Oxygen-Containing Organic Compounds

BY HARUKA YAMADA AND KUNIO KOZIMA

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When iodine was added to solutions of various oxygen-containing organic compounds, shifts of the infrared absorption bands and changes in the intensities of the bands were observed. These shifts may indicate the formation of complexes between iodine and the solutes. In the case of the ketone-iodine complexes, the intensities of the bands assigned to the C=O stretching vibrations of the ketones increased remarkably, while in the case of the ethyl ether-iodine complex, the intensity of the band assigned to one of the C-O stretching vibrations of ethyl ether decreased. The charge-transfer from the oxygen atoms to iodine molecules and the change in the ionicity of the donating groups, caused by the transfer, may account for most of these phenomena. Although methyl acetate and 3-phenylsindone possess two or more atoms having lone-pair or π -electrons, iodine combines only with the carbonyl group. For each system the formation constant of the 1:1 complex was determined.

It is well known that molecular complexes are formed between iodine and various organic compounds having lone-pair or π -electrons.^{1,2} The

(1) R. S. Mulliken, *THIS JOURNAL*, **72**, 600 (1950); *ibid.*, **74**, 811 (1952); *J. Phys. Chem.*, **56**, 801 (1952).

bond between them may be due mainly to a charge-transfer force. Although the existence of the molecular complexes frequently is detected by the

(2) L. J. Andrews, *Chem. Revs.*, **54**, 713 (1954); S. P. McGlynn, *ibid.*, **58**, 1113 (1958).