The Thermal Decomposition and Reduction of Silver(I) Oxide

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The thermal decomposition of silver(I) oxide and its reduction with reductive gases, such as ethylene, hydrogen, and carbon monoxide, have been studied by using a fixed-bed flow reactor. Under isothermal conditions, each reaction gave a sigmoidal shape to the fractional decomposition *vs.* time curves, and these curves were in good agreement with Avrami's equation. The temperature at which the reaction commenced corresponded well to the chemical affinity of the reaction, and a linear free-energy relationship holds between the apparent activation energy and the standard enthalpy change of the reaction. In the thermal decomposition, an enlargement in particle size resulting from the melting and sintering of the product silver was recognized, but in the reduction the particle size scarcely varied during the reaction. On the basis of these results, the mechanism of each reaction was discussed.

The thermal decomposition of silver(I) oxide has been investigated by various workers, but no reasonable explanation of the decomposition rate equation and the reaction mechanism were obtained. With regard to the fractional decomposition (α) *vs.* reaction time (t) curves, both sigmoidal and nonsigmoidal curves have been reported. Sigmoidal curves have been reported by Lewis$^{1)}$ and by Hood and Murphy,$^{2)}$ who proposed that the reaction proceeded autocatalytically obeying by Ostwald's equation: $d\alpha/dt=k\alpha(1-\alpha)$. Recently, Tobisawa$^{3)}$ and Herley and Prout$^{4)}$ have proposed a topochemical approach to these observed sigmoidal curves. Nonsigmoidal curves which have a maximum rate at the initial stage of the decomposition have been reported by Pavluchenko and Gurevich$^{5)}$ and by Garner and Leaves.$^{6)}$ Kato *et al.*$^{7)}$ observed nonsigmoidal curves which showed that the reaction proceeded linearly with the time up to a great extent of the fractional decomposition. However, almost all the samples which have not shown sigmoidal curves have undergone grinding or preheating. These treatments may have an effect on the physical and chemical properties of the samples.

On the other hand, the reduction of silver oxide with ethylene has been studied in order to examine the role of silver as a catalyst in the direct oxidation of ethylene.$^{8-10)}$ Kagawa *et al.*$^{9)}$ found that, both in the thermal decomposition of silver oxide and in its reduction with ethylene, the reactions proceeded obeying Ostwald's equation and suggested that the two mechanisms of reactions were similar.

In this paper, on the basis of a comparison of the thermal decomposition with the reduction with several reductive gases, the reaction mechanisms will be discussed.

Experimental

Preparation of Silver(I) Oxide. The sample of silver oxide was prepared from silver nitrate and sodium hydroxide. In order to eliminate the silver carbonate formed at the surface of the silver oxide, the specimen was treated in a carbon dioxide-free nitrogen stream at 60—120 °C for 48—72 hr and stored *in vacuo* over silica gel under dark-room conditions. By a chemical analysis of the silver, the sample gave 100±0.2% as silver(I) oxide and was confirmed gas-chromatographically not to evolve oxygen gas below 250 °C, while the X ray diffraction patterns did not show any line of silver or of silver carbonate.

Apparatus and Procedure. The reaction was carried out in a fixed-bed flow reactor using a Pyrex tube 1 cm in inside diameter. A given amount of the silver oxide sample was packed in the reactor. In the case of the thermal decomposition, the nitrogen used as a carrier gas was passed through at a constant flow rate. The reactor was immersed in a fused-salts bath and heated; then the reaction commenced. The product oxygen in the effluent gas was analyzed by gas-chromatography. The reaction rate was determined from the flow rate of the carrier gas and from the oxygen concentration in the effluent gas. In the cases of the reductions with ethylene, hydrogen, and carbon monoxide, pure reactant gases and mixtures of them with nitrogen gas were passed through the reactor at a constant flow rate and the reaction product gases, such as ethylene oxide, carbon dioxide, and water vapour, were analyzed gas-chromatographically. In each reduction, no oxygen gas evolution as a result of the thermal decomposition was detected. One of the baths of the oil, the water or the water-methanol, was selected as a thermostat according to the reaction temperature.

Experiments were carried out both isothermally and dynamically. In the case of a dynamical operation, the heating rate was 2 °C/min. In the case of an isothermal operation, the required temperature could be obtained within 5 minutes and the temperature was controlled within ±0.5 °C during the course of the reaction. At slow flow rates up to 80 cm^3/min, the effect of the flow rate on the rates of the thermal decomposition and the reduction was observed. Therefore, experiments were carried out at flow rates above 80 cm^3/min. The sample weight did not effect the reaction rate. Considering the accuracy of analysis and the elimination of the heat of reaction, the sample weight was determined to be 0.5—1.5 g for the thermal decomposition and for the reduction with ethylene, and about 0.15 g for the reductions with hydrogen and carbon monoxide.

Results

Reaction under Dynamical Conditions. As is shown in Fig. 1, the thermal decomposition of silver oxide began at 330 °C, reached a maximum rate at about 440 °C, and was completed at 500 °C. On the other hand, the reduction with ethylene occurred over the range of temperature of 110—210 °C, that with hydrogen, at 10—130 °C, and that with carbon monoxide, at −40—30 °C. By balancing the oxygen atoms in

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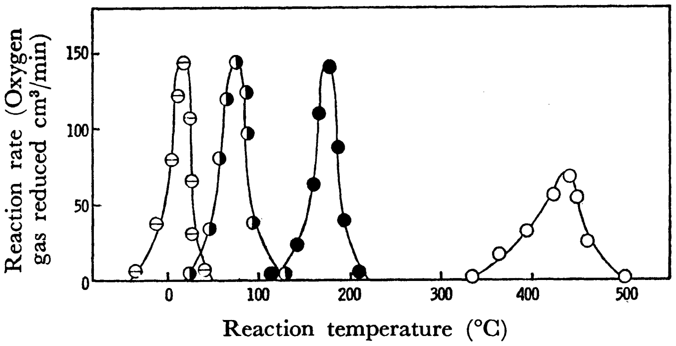

Fig. 1. Reaction under dynamical condition (heating rate 2 °C/min). ⊖ reduction with CO, ● reduction with C_2H_4, ◑ reduction with H_2, ○ thermal decomposition in N_2.

Table 1. Oxygen balance and reaction equation

System	O in sample a(mg)	O in product b(mg)	O balance b/a	Reaction equation	ΔG°_{298} (kcal/mol)	T_c (°C)
Ag_2O-N_2	34.2	35.2	1.03	$Ag_2O \rightarrow 2Ag + \frac{1}{2}O_2$	2.6	330
Ag_2O-C_2H_4	33.6	34.9	1.04	$Ag_2O + C_2H_4 \rightarrow 2Ag + C_2H_4O$ $Ag_2O + \frac{1}{6}C_2H_4 \rightarrow 2Ag + \frac{1}{3}CO_2 + \frac{1}{3}H_2O$	−44.5	110
Ag_2O-H_2	33.8	34.9	0.97	$Ag_2O + H_2 \rightarrow 2Ag + H_2O$	−54.5	10
Ag_2O-CO	35.8	35.2	0.98	$Ag_2O + CO \rightarrow 2Ag + CO_2$	−58.7	−40

product gases with those in silver oxide used, the reaction equations were determined. The results are shown in the fifth column of Table 1. In the reduction of silver oxide with ethylene, two reactions occurred competitively and the selectivity of ethylene oxide based on the ethylene reacted was about 37%. In the sixth and seventh columns of Table 1 respectively, the temperature at which the reaction commenced (T_c) and the standard free energy change of the reaction (ΔG°_{298}) are described. Between T_c and ΔG°_{298} a fairly good correspondence is found; the smaller (the more negative) the ΔG°_{298}, the lower the T_c.

Reaction under Isothermal Conditions. The thermal decomposition under isothermal conditions was carried out between 410—430 °C. The fractional decomposition *vs.* time curves are shown in Fig. 2. These curves, which showed an accelerated period, gave a sigmoidal shape characteristic of a solid reaction. The reductions of silver oxide with ethylene, hydrogen, and carbon monoxide were carried out at the temperature ranges of 136—145 °C, 65—75 °C, and −8—10 °C respectively. The results[11)] are shown in Figs. 3, 4 and 5. Although the reaction temperatures were different from each other, the shapes of the curves were sigmoidal, similar to those of the thermal decomposition in nitrogen.

In the case of the reduction with ethylene, the effect of the partial pressure of ethylene on the reduction rate is illustrated in Fig. 6.[12)] The partial pressure of

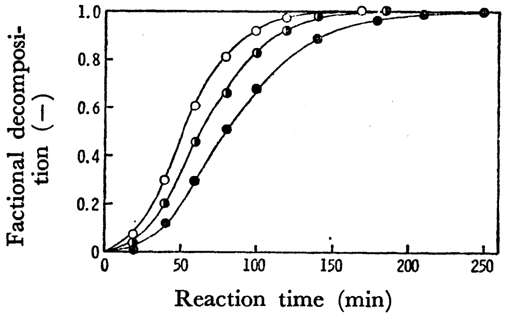

Fig. 3. Reduction with C_2H_4.
○ at 145 °C, ◑ at 140 °C, ● at 136 °C

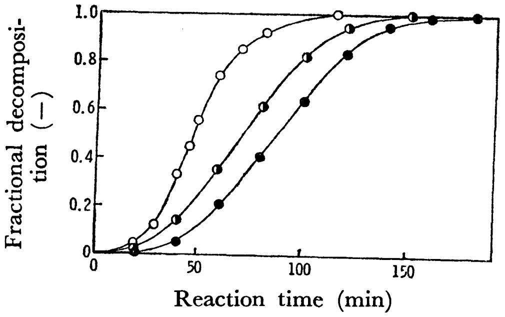

Fig. 2. Thermal decomposition in N_2.
○ at 430 °C, ◑ at 420 °C, ● at 410 °C

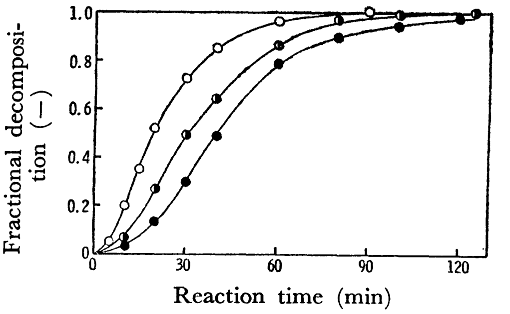

Fig. 4. Reduction with H_2.
○ at 75 °C, ◑ at 70 °C, ● at 65 °C

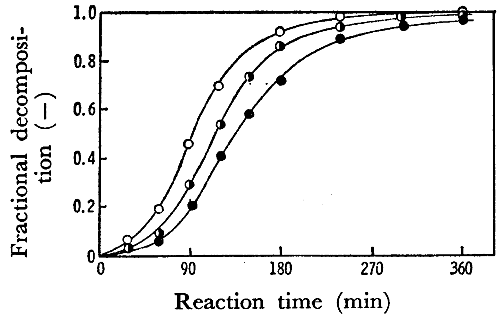

Fig. 5. Reduction with CO.
○ at 10 °C, ◑ at 0 °C, ● at −8 °C

ethylene below 0.4 atm had a considerable influence on the reaction rate constant, but above 0.4 atm the effect was negligible. For the other reductive gases, similar results were obtained.

Scanning-Electron-Microscope Observation. The sample of silver oxide consisted of opaque polycrystalline particles. From scanning electron micrographs it was observed that some dozens of primary particles about 0.1 μ in size aggregate to form a secondary particle several ten microns in size. Some examples of scanning electron micrographs are shown in Fig. 7. In the case of the thermal decomposition, the product silver somewhat melted in the course of the reaction. After the completion of the decomposition, the particle size of silver came to about several ten times larger than that of the sample of silver oxide.

On the other hand, in the case of the reduction, the primary particle decreased in size as the density changed from oxide to metallic silver, and no enlargement in size as a result of sintering was observed. From this result an enlargement in size resulting from the aggregation or sintering of primary particles does not seems to affect the fractional decomposition *vs.* time curves or, therefore, the reaction mechanism.

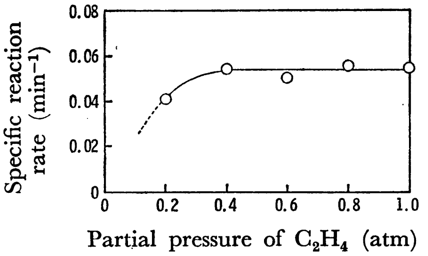

Fig. 6. Effect of partial pressure of C_2H_4 on reaction rate at 138 °C.

Discussion

The overall reaction of the thermal decomposition and reduction of silver(I) oxide can be written commonly by this equation:

$$Ag_2O(\text{solid}) + \text{Reactant(gas)} \rightarrow Ag(\text{Solid}) + \text{Product(gas)} \qquad (1)$$

In the thermal decomposition, there is nothing corresponding to the reactant in Eq. (1), and the product is oxygen. The results in these experiments showed that, in a series of reactions, the thermal decomposition

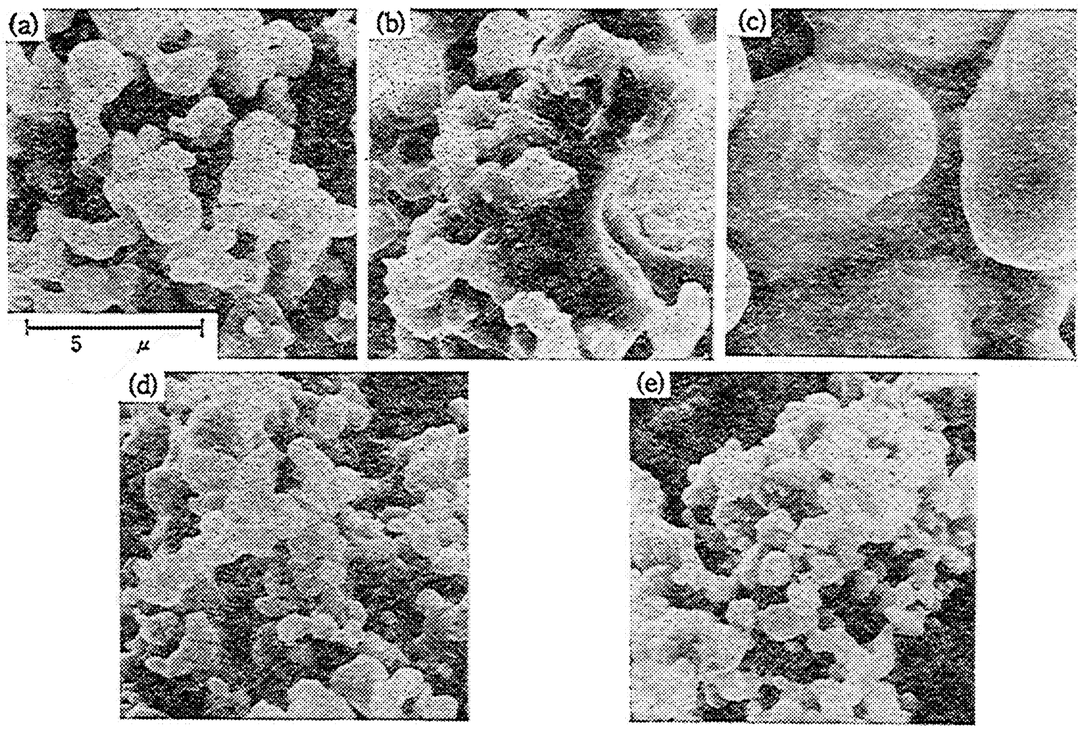

Fig. 7. Scanning electron micrographs of some selected samples.

a) Silver(I) oxide undecomposed. b) Sample at fractional decomposition of 0.5 in the thermal decomposition. c) Sample at complete decomposition in the thermal decomposition. d) Sample at fractional decomposition of 0.5 in the reduction with C_2H_4. e) Sample at complete decomposition in the reduction with C_2H_4.

occurred at the highest temperature (330 °C) and that the reduction with carbon monoxide occurred at the lowest temperature (−40 °C). The temperature at which the reaction commenced varied approximately linearly with ΔG°_{298}. It is interesting that each of these reactions gave the same sigmoidal shape to the fractional decomposition *vs.* time curves, although these reactions occurred at different temperatures, extending over a wide range.

Two kinds of theories to explain sigmoidal curves in a phase transformation and a thermal decomposition have been proposed. One kind is exemplified by those of Garner and of Prout and Tompkin, which explain the growth of nuclei in terms of the branching chain-reaction mechanism; the other kind is exemplified by Avrami, Mampel, Erofeev, and Cahn's theories, which take into account the overlapping of growing nuclei. Prout and Tompkin's rate equation is identical with Ostwald's equation, which was used by Lewis and by Hood and Murphy. However, it is unreasonable to apply this equation over the entire range of decomposition, because an equation of this form requires that all the solid product be in a position to catalyse all the particles of the solid reactant equally throughout the complete course of the reaction. In a solid decomposition where the mobility of the reacting constituents is low, such a situation is not feasible.[13] Besides, the results of this experiment did not fit in well with Prout-Tompkin's equation.

On the other hand, the latter contains complicated equations, none of which can be applied to any practical problem. However either of the following approximate equations can be utilized:

$$\alpha/(1-\alpha) = Bt^k \tag{2}$$

$$\alpha = 1 - \exp(-Bt^k) \tag{3}$$

where α is the fractional decomposition; t, the reaction time, and B and K, the constants characteristic of the reaction system.

As is shown in Figs. 8—11, the present experimental results fit in well with Eq. (3) except in the case of the

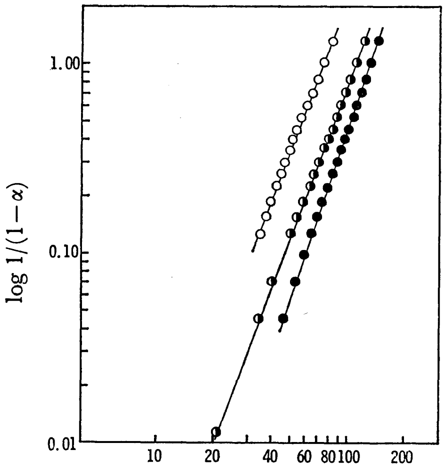

Fig. 8. Avrami plot in the case of thermal decomposition.
○ at 430 °C, ◑ at 420 °C, ● at 410 °C

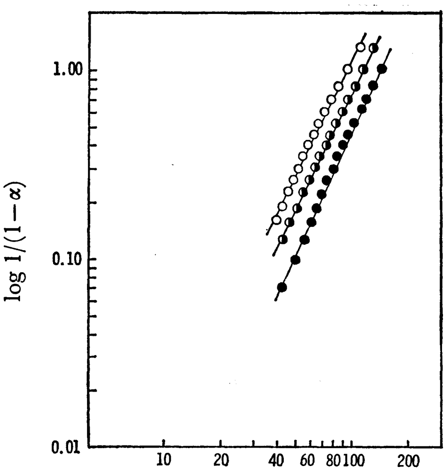

Fig. 9. Avrami plot in the case of reduction with C_2H_4.
○ at 145 °C, ◑ at 140 °C, ● at 136 °C

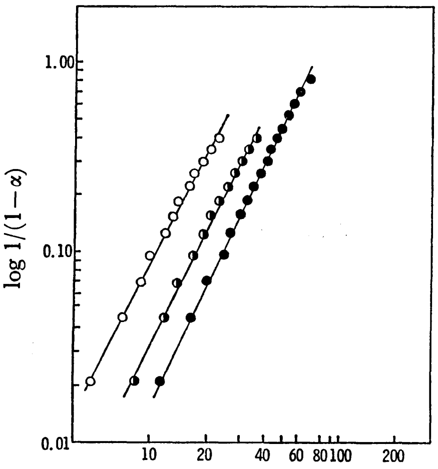

Fig. 10. Avrami plot in the case of reduction with H_2.
○ at 75 °C, ◑ at 70 °C, ● at 65 °C

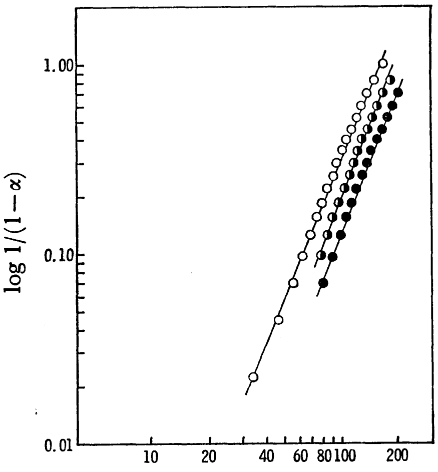

Fig. 11. Avrami plot in the case of reduction with CO,
○ at 10 °C, ◑ at 0 °C, ● at −8 °C

TABLE 2. EXAMINATION OF VALIDITY TO AVRAMI'S EQUATION AND APPARENT ACTIVATION ENERGY

System	Reaction temperature (°C)	k	B	Applicable range of Avrami's equation	E_a (kcal/mol)
Ag_2O-N_2	430	2.75	17.36×10^{-6}	$0.25<\alpha<0.95$	
(thermal decompn.)	420	2.61	8.67×10^{-6}	$0.03<\alpha<0.95$	96.5
	410	2.81	2.32×10^{-6}	$0.10<\alpha<0.95$	
Ag_2O-C_2H_4	145	2.04	2.15×10^{-4}	$0.30<\alpha<0.95$	
	140	2.08	1.22×10^{-4}	$0.25<\alpha<0.95$	38.5
	136	2.17	0.67×10^{-4}	$0.15<\alpha<0.95$	
Ag_2O-H_4	75	2.00	8.31×10^{-4}	$0.05<\alpha<0.60$	
	70	2.00	7.45×10^{-4}	$0.05<\alpha<0.60$	24.8
	65	2.10	2.90×10^{-4}	$0.05<\alpha<0.85$	
Ag_2O-CO	10	2.44	9.51×10^{-6}	$0.05<\alpha<0.90$	
	0	2.61	2.70×10^{-6}	$0.15<\alpha<0.95$	16.2
	−8	2.68	1.30×10^{-6}	$0.10<\alpha<0.80$	

reduction with hydrogen, where the range of applicability of Eq. (3) is somewhat small. From these figures, the values of k and B were determined. They are shown in Table 2. The values of k, being within 2.00—2.81, were approximately constant in all the reaction systems. From the finding that the thermal decomposition and the reduction occur obeying the same rate equation, it can be considered that the rate-determining step is similar. Plots of log B against $1/T$ (K^{-1}) gave straight lines, and from their slopes the apparent activation energies (E_a) were determined. The plot of this activation energy against the standard enthalpy change of the reaction at the average temperature investigated (ΔH_T°) gave a fairly good straight line (Fig. 12). Let us now discuss this free-energy relationship.

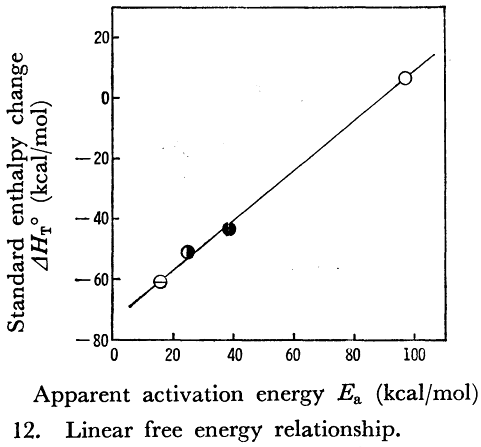

Fig. 12. Linear free energy relationship.
⊖ reduction with CO, ◑ reduction with H_2, ● reduction with C_2H_4. ○ thermal decomposition in N_2

Although the mechanism of Reaction (1) is not yet known in detail, generally the following steps may be considered: Silver oxide decomposes at the active point which exists in the interior of crystal or on the surface layer, thus producing silver and oxygen atoms. Then this oxygen atom diffuses to the outer surface to react with the reactant gas, and the silver atom diffuses to the interface between metallic silver and silver oxide to form a silver crystal.

Since the fractional decomposition *vs.* time curves gave a sigmoidal shape, the diffusion step may not be the rate-determining step. If the chemical reaction of an oxygen atom with a reactant gas occurs at the surface of silver oxide, the reaction rate depends upon the surface area of the silver oxide and on the partial pressure of the reactant gas. Since the surface area of silver oxide decreases as the reaction proceeds, the reaction rate must decrease monotonously and does not have an accelerated period. Even if this chemical reaction occurs over the whole surface of both silver oxide and silver, the sigmoidal curves cannot be explained, for the total surface area either remains constant (in the case of the reduction) or decreases gradually (in the case of the thermal decomposition), as may be seen in scanning electron micrographs. Moreover, the rate of the reaction is not first-order with respect to the partial pressure of reductive gas. Thus, the chemical reaction may not be the rate-determining step.

From Allen's[14]) study it is reasonable to consider that silver-oxygen bond secession occurs at the initial stage of the reaction. However this step may not be the rate-determining step, for if it is so, the activation energies of each reaction must be constant in all the reaction systems, while in reality the apparent activation energy of each reaction, as calculated from the initial reaction rate, varied with the reaction system–the higher the reaction temperature, the larger this value.

Dubinin *et al.*[15]) and Kato *et al.*[7]) have reported that the thin layer silver coating on silver oxide and silver produced by the reduction with ethylene considerably increases the reaction rate. From these reports, and the finding that a series of these reactions occur obeying the same rate equation, similar to the equation of an ordinary phase transformation, it is more reasonable to consider that the step of the nucleation of silver- and its development is the rate-determining step.

Though the results of this experiment can not reveal the detailed reaction mechanisms, from the above considerations we can estimate Eqs. (4) and (5) to be:

$$Ag_2O(\text{solid}) + \text{Reactant(gas)} \rightarrow Ag(\text{interface}) + \text{Product(gas)} \qquad (4)$$

$$Ag(\text{interface}) \rightarrow Ag(\text{solid}) \qquad (5)$$

From the previous discussion it can be considered that Reaction (4) steadily occurs in a preliminary equilibrium, and that Reaction (5) is rate-determining. Therefore:

$$\Delta G^\circ_{(1)} = \Delta G^\circ_{(4)} + \Delta G^\circ_{(5)} \qquad (6)$$

$$\Delta G^\circ_{(4)} = -RT\ln(C_{Ag}\cdot C_{prod.}/C_{react.}) \qquad (7)$$

The B is Avrami's rate equation is some function of the formation rate of the nuclei ($\dot{N}$) and the growth rate of the nuclei (G).[16] Though the form of this function depends upon the dimensionality of the development of the nuclei, in general it takes the form of const$\cdot G^a\cdot \dot{N}^b$.

The volume nucleation rate is approximately[16]:

$$\dot{N}_j = \nu n(\delta/D)^{3-j}\exp\{-(\Delta G_j^{\neq}+\Delta G_A^{\neq})/RT\} \qquad (8)$$

where j is the dimensionality of the nucleation site; ν, a frequency factor; n, the number of atoms per unit volume; δ, an effective grain boundary thickness; D, the grain diameter; $\Delta G_j^{\neq}$, the minimum free energy required to form a nucleus, and $\Delta G_A^{\neq}$, the free energy of activation for a nucleus to continue to grow.

The linear growth rate would be:

$$G = \nu\delta(n/s)\exp(-\Delta G_A^{\neq}/RT) \qquad (9)$$

where n/s is the density of atoms per unit area of the reactive molecules.

By rearranging Eqs. (1), (4) and (5), we get:

$$C_{Ag} = (C_{react.}/C_{prod.})\exp\{-(\Delta G^\circ_{(1)}-\Delta G^\circ_{(5)})/RT\} \qquad (10)$$

where C_{Ag} is the concentration of silver atoms and is proportional to n.

Since the experiments in this study were carried out under similar conditions, the values of ($C_{react.}/C_{prod.}$) during the course of the reaction are equal in each reaction; thus, the apparent activation energy obtained from the Arrhenius plot of B becomes:

$$E_a = b\Delta H_j^{\neq} + (a+b)(\Delta H_A^{\neq}+\Delta H^\circ_{(1)}-\Delta H^\circ_{(5)}) \qquad (11)$$

where ΔH° is an enthalpy change term corresponding to a free-energy change term. Since $\Delta H_j^{\neq}$, $\Delta H_A^{\neq}$, and $\Delta H^\circ_{(5)}$ are considered to be constant in all the reaction systems, we can understand that the plot of the apparent activation energy against $\Delta H^\circ_{(1)}$ should be a straight line.

From the above discussion, we may conclude that, since the chemical reaction process is very rapid, and since the process of the crystallization of new-phase silver is the rate-determining step, the thermal decomposition and reduction of silver oxide show the same kinetic behaviour as a phase transformation.

About the thermal decomposition of silver oxide, Allen[14] reported that the activation energy calculated from the reaction rate and the reaction temperature was 36 kcal/mol. A differentiation of Eq. (3) with t yields:

$$d\alpha/dt = kB^{1/k}f(\alpha) \qquad (12)$$

Thus, the activation energy determined by Allen must be equal to $1/k$ times our apparent activation energy. Actually, the two give approximately equal values.

In this study, it is difficult to discuss the sites of nucleation and the dimensionality of the growth of the nuclei in detail considering the accuracy of our experiments. Moreover, whether or not the sites where the bond secession of silver oxide occurs are identical with the sites where the nuclei of a silver crystal generates is an interesting problem for future study.

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