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Thermal Decomposition of Gadolinium-Doped Silver Carbonate

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A thermogravimetric analysis (TGA) study of the decomposition kinetics of gadolinium-doped silver carbonate is reported. The TGA data were used to obtain the activation energy, pre-exponential factor, and order of reaction by the method of Ozawa. Powdered samples were found to obey a first-order rate law from 10 to 90% decomposition. Neither an induction nor an acceleratory period was observed. By decomposing pressed pellets the interface mechanism for the decomposition of Gd-doped silver carbonate was confirmed. Water vapor catalyzed the decomposition, and water incorporated in the crystal lattice during sample preparation may partly account for the high reactivity of Gd-doped silver carbonate. Values for the pre-exponential factor and the activation energy with and without water vapor revealed an apparent compensation effect. The activation energy, 21.4 kcal/mole, for decomposition of Gd-doped silver carbonate in the presence of water vapor agreed favorably with the heat of reaction, suggesting that the recombination of doped silver oxide and carbon dioxide requires little or no energy of activation. The model proposed by Barnes and Stone to describe the decomposition of active silver carbonate is related to the findings with Gd-doped silver carbonate.

INTRODUCTION

In a continuing research program (*1*) on the influence of additives or dopants on the kinetics and mechanisms of the thermal decomposition of silver carbonate, the work has been extended to gadolinium-doped silver carbonate. Gadolinium was chosen as the dopant for this study because at ratios of gadolinium to silver ≥ 0.5 at. %, the crystal structure of silver carbonate was different from undoped monoclinic silver carbonate (*2*). The X-ray diffraction powder patterns of the new structure appeared identical to yttrium-doped silver carbonate at comparable dopant concentrations. It was therefore of interest to investigate the thermal decomposition kinetics of gadolinium-doped silver carbonate (Gd–Ag_2CO_3) to compare the results with both yttrium-doped and undoped silver carbonate.

METHODS

Gadolinium nitrate hexahydrate (American Potash and Chemical Corp., stated purity with respect to other rare earths, 99.99%) and analytical grades silver nitrate and sodium carbonate were used as starting materials to prepare ~1 mole % gadolinium carbonate-doped silver carbonate. The sample was prepared, filtered, and dried, using the same techniques as described previously for preparing yttrium-doped silver carbonate (*1*). The dried powder was sieved and the −115 +325 sieve fraction was selected for subsequent experiments.

Analysis of the dried powder gave the following results: Constituent (wt %): Ag, 76.45; Gd, 1.13; CO_3^{-2}, 21.80; H_2O, 1.23; and NO_3^-, 0.020.

Estimates of the particle size of the powder were made using electron micrographs as well as a modified version of the Fisher Sub-Sieve Sizer. The BET surface area measurements were made using nitrogen with the assumption that 16.3Å^2 is the area occupied by the nitrogen molecule. The electron micrographs revealed relatively uniform size agglomerates of circular crystallites (in two dimensions) having a diameter of about 4.0×10^{-6} cm. Using the Fisher Sub-Sieve Sizer the measured particle diameter was 1.28×10^{-4} cm, which is expected to be the approximate diameter of the agglomerates. The value derived from the Sub-Sieve Sizer was calculated by using the tightest packing manually obtainable and assuming a particle density of 6.08 g/cm^3 (bulk density of undoped silver carbonate). The particle diameter calculated from the BET surface area, 12.3 m^2/g, and assuming the particles were spherical, was 8.02×10^{-6} cm, which is comparable to the diameter of the crystallites derived from the electron micrographs.

Thermogravimetric analysis data were gathered using a Perkin-Elmer TGA system in conjunction with a strip chart recorder. Purified nitrogen (stated purity 99.99%) flowed over the sample at about 30 ml/min during an experiment. To study the influence of water vapor on the rate of decomposition of Gd–Ag$_2$CO$_3$, nitrogen was passed through a gas bubbler containing a saturated solution of magnesium nitrate before flowing over the sample. The partial pressure of water vapor in the nitrogen was checked with an Alnor Dewpointer. The expected partial pressure, 13 mm Hg, based on the water vapor pressure over a saturated solution of magnesium nitrate at 25°C was comparable to the measured partial pressure, 11 mm Hg. The average amount of the powdered samples used for the TGA runs was 6 mg.

Infrared spectra in the region from 400 to 4000 cm^{-1} were obtained with a Beckman IR-9 spectrophotometer, which was continuously purged with dry air and operated in the single beam mode. The slit width was varied from 1.5 to 3 mm depending on the region of the spectrum being studied. The IR samples were in the form of either undiluted pellets or Nujol mulls. Undiluted pellets (13-mm diam.) of Gd–Ag$_2$CO$_3$ were pressed under vacuum at 5700 kg/cm^2. Mulls were prepared using Nujol and a small amount of sample.

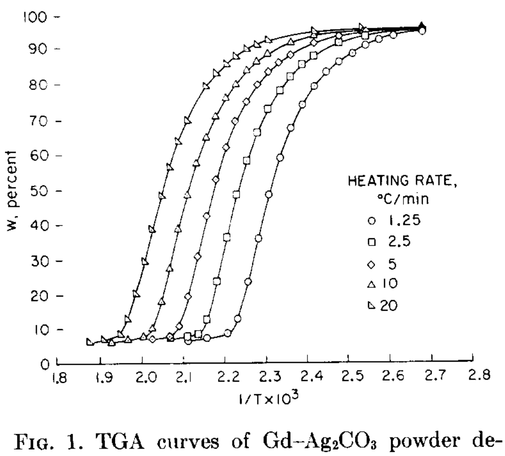

FIG. 1. TGA curves of Gd–Ag$_2$CO$_3$ powder decomposed under a nitrogen + water vapor atmosphere; p_{H_2O} = 11 torr.

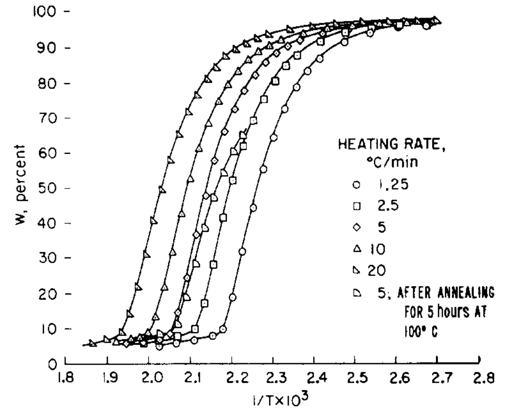

FIG. 2. TGA curves of Gd–Ag$_2$CO$_3$ powder decomposed under a dry nitrogen atmosphere; (△), TGA run at 5°C/min after annealing for 5 hr in dry nitrogen at 100°C; 22% decomposition occurred at 100°C prior to the start of the TGA run.

RESULTS AND DISCUSSION

Thermogravimetric analysis runs on ~1 mole % (excluding moles of water) gadolinium carbonate-doped silver carbonate powder decomposed under dry nitrogen and a nitrogen plus water vapor atmosphere are shown in Figs. 1 and 2. The integral method described by Ozawa (*3*) and more recently reviewed favorably by Flynn and Wall (*4*) was used to obtain the activation energy, order of reaction, and pre-exponential factor from the TGA data, Figs. 1 and 2.

The activation energies for powder decomposed under dry N$_2$ and a N$_2$ + water vapor atmosphere, Table 1, were obtained from the slopes of semilog plots of the heating rate, a, versus the reciprocal of the absolute temperature, T, at a constant residual mole percent doped silver carbonate, W.

The experimental master thermogravimetric curves, Fig. 3, were constructed by superposition of the curves at heating rates of 1.25, 2.5, 10, and 20°C/min on the curves at 5°C/min. By taking values of W at given temperatures from the experimental master thermogravimetric plots and using the aver-

TABLE 1

KINETIC PARAMETERS FOR THE THERMAL DECOMPOSITION OF Gd–Ag_2CO_3 POWDER

	Without H_2O vapor		With H_2O vapor	
W (%)	E (kcal/mole)	$A \times 10^{-8}$ (sec^{-1})	E (kcal/mole)	$A \times 10^{-8}$ (sec^{-1})
90	24.8 (2.3)[b]	14.28[a]	21.0 (2.2)[b]	0.846[a]
85	—	10.61	—	0.667
80	24.5 (1.8)	9.35	21.4 (2.4)	0.590
70	24.3 (2.2)	8.31	21.6 (2.2)	0.535
60	24.3 (2.4)	7.84	21.6 (2.1)	0.517
50	24.2 (2.2)	7.58	21.6 (2.0)	0.519
40	24.1 (2.3)	7.62	21.9 (2.4)	0.532
30	24.1 (2.0)	7.71	21.3 (1.6)	0.554
20	23.6 (1.7)	7.94	21.4 (1.5)	0.581
10	23.5 (2.3)	7.99	21.2 (1.2)	0.615
8	—	6.50	—	—
7.5	—	—	—	0.421
Av	24.2	8.15	21.4	0.553

[a] These values were rejected with 90% confidence in computing the average.

[b] Numbers in parentheses represent the uncertainty for a 95% confidence interval.

age activation energy, Table 1, values of the function $\log[(E/aR)p(E/RT)]$ (*3*) were computed and plots of W against

$$\log[(E/aR)p(E/RT)]$$

were constructed. Values for the function $p(E/RT)$ were taken from Doyle (*5*). The plotted curves were then compared with the theoretical thermogravimetric curves plotted by Ozawa (*3*) for zero-, first-, second-, and third-order reactions. This comparison showed that the shape of the curve for the powder decomposed under either a dry N or N_2 + water vapor atmosphere agreed best with the shape of the theoretical curve for a first-order reaction.

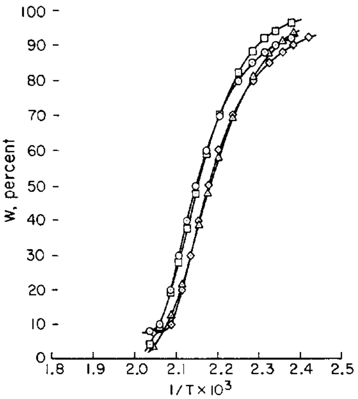

FIG. 3. Comparison between the master experimental thermogravimetric curves and derived TGA curves for the decomposition of Gd–Ag_2CO_3 powder; heating rate 5°C/min: master curve, dry N_2 atmosphere (○); derived curve, dry N_2 atmosphere (□); master curve, 11 torr water vapor + N_2 atmosphere (◇); and derived curve, 11 torr water vapor + N_2 atmosphere (△).

The pre-exponential factors, A, Table 1, for the first-order reaction with respect to doped silver carbonate were then calculated using the following equation:

$$\log A = \log[-2.303 \log W] - \log\left[\left(\frac{E}{aR}\right) p\left(\frac{E}{RT}\right)\right], \quad (1)$$

where $a = 5°C/min$ and $E = 24.2$ kcal/mole without water vapor present and 21.4 kcal/mole with water vapor. The W versus $1/T$ values were taken from the master experimental thermogravimetric curves, Fig. 3.

Using the derived values for A, E, and the reaction order, the first-order rate equations for the thermal decomposition of Gd–Ag_2CO_3 are:

$$-\frac{dW}{dt} = 8.15 \times 10^8 \exp(-24200/RT)W$$

[fraction of carbonate decomposed/sec], (2)

$$-\frac{dW}{dt} = 5.53 \times 10^7 \exp(-21400/RT)W \quad (3)$$

without and with water vapor present, respectively.

By rearranging Eq. (1) and substituting for a, E, A, and R, the following equations were derived:

$$-\log W = 5.16 \times 10^{13} p \left(\frac{E}{RT}\right), \tag{4}$$

$$-\log W = 3.11 \times 10^{12} p \left(\frac{E}{RT}\right) \quad \text{(with water vapor)}, \tag{5}$$

where W = residual fraction of doped silver carbonate. Equations (4) and (5) were used to compute values of W at selected temperatures and plots of W versus $1/T$ were constructed for a heating rate of 5°C/min, Fig. 3. The derived thermogravimetric curves compare favorably with the master experimental thermogravimetric curves over the interval W = 10 to 90% carbonate without further refinement of the parameters A and E. The constancy of A and E, within experimental error, over the interval from W = 10 to about 90% shows that the reaction mechanism does not change within this interval either with or without water vapor, Table 1.

If Gd–Ag$_2$CO$_3$ behaves similarly to yttrium-doped silver carbonate and undoped silver carbonate, then the rate of decomposition should be proportional to the number of surface sites (*1*, *6*), i.e., the Polanyi-Wigner equation (*7*) should be obeyed. Agreement between the experimental and the Polanyi-Wigner rates also implies that the solid decomposes by the interface mechanism. Using the following form of the Polanyi-Wigner equation:

$$-\frac{dN}{dt} = A'\nu\tilde{N}\exp(-E/RT), \tag{6}$$

and substituting the following values for the variables: A' = 737 cm^2 (area of the interface); $\tilde{N} = 2.33 \times 10^{14}$ molecules of carbonate/cm^2 surface; $\nu = 5 \times 10^{12}$ sec^{-1} (*7*); E = 21.4 kcal/mole (activation energy for migration of the interface); T = 431°K; the predicted decomposition rate for powder *in the presence of water vapor* is 1.17×10^{19} molecules/sec. The value for A' was obtained from the BET surface area and the initial sample weight, 5.999 mg. If instead of using the BET surface area the cross-sectional area of the aluminum sample container, 0.113 cm^2, is substituted as an approximation for A' then the predicted rate is 1.80×10^{15} molecules/sec which agrees favorably with the experimental rate, 1.03×10^{16} molecules/sec. The experimental rate was obtained from the slope of the tangent drawn to the curve of W versus time, Fig. 4, at a small extent of reaction, i.e., when the interface is least disturbed by decomposition. The decomposition rate of yttrium-doped silver carbonate powder in the presence of water vapor also was proportional to the cross-sectional area of the crucible (*1*).

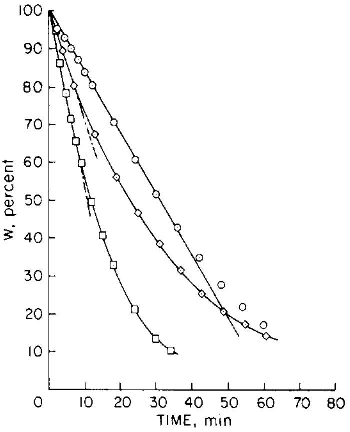

FIG. 4. Isothermal decomposition curves at 158°C for Gd–Ag$_2$CO$_3$ powder and a pressed pellet: powder, dry N$_2$ atmosphere (◇); powder, 11 torr water vapor + N$_2$ atmosphere (□); pellet, 11 torr water vapor + N$_2$ atmosphere (○); and (——), tangents used for obtaining experimental rates at W = 100% to compare with predicted rates using the Polanyi-Wigner equation.

It should be noted that the relative sample size used in the present study was 25 times less (6 versus 150 mg), and the relative cross-sectional area of the crucible was only 4.5 times smaller (0.113 versus 0.502 cm^2) (*1*) This suggests that for the experimental decomposition rate to be proportional to the BET surface area, it would be necessary to use essentially a monolayer of powder in the crucible. It is not only difficult to obtain a monolayer of the very small crystallites from the agglomerates, but also larger errors arise in acquiring TGA data with very small samples.

Without water vapor present the experimental rate for the powder was 6.34×10^{15}

molecules/sec (see Fig. 4) and the predicted rate 7.57×10^{13} molecules/sec using the crucible cross-sectional area. Agreement between the experimental and predicted rates is within two orders of magnitude thus suggesting the interface mechanism also applies in this case (*8*).

The apparent contradiction between the applicability to the experimental data of both the first-order rate law, which implies random nucleation, and the Polanyi-Wigner equation, which implies the interface mechanism, can be explained as follows. The agreement between the first-order rate law and the experimental data may be fortuitous because of the complex geometry of the powder interface. The low values for the pre-exponential factors (much less than 10^{13} sec^{-1}), Table 1, indeed strongly suggests that the decomposition reaction is not a true but rather a pseudo first-order reaction.

To aid in verifying the interface mechanism and overcome the problem of complex surface geometry, the powder was pressed into 13-mm diameter pellets and a small part of the pellet was used for a TGA experiment. If the interface mechanism applies then the decomposition rate should be essentially constant (neglecting decomposition from edges) for thin pellets (0.016-mm thick) and proportional to the geometric surface area of the pellet. Figure 4 shows that the decomposition rate of the pelletized sample in the presence of water vapor is indeed constant, within experimental error, from $W = 100$ to 35%. Retention occurs for $W < 35\%$ (*9*). The experimental rate calculated from the slope of the pellet decomposition curve, Fig. 4, is 3.79×10^{15} molecules/sec. The decomposition rate predicted using Eq. (6) is 3.25×10^{15} molecules/sec. The geometric area of the pellet was 0.205 cm^2. Values for E and $\tilde{N}$ were the same as those chosen previously for predicting a reaction rate for powder decomposed in the presence of water vapor. It appears therefore that the interface mechanism does indeed apply to the decomposition of Gd–Ag_2CO_3.

Barnes and Stone (*10*) recently proposed a model to explain the high reactivity of undoped silver carbonate containing water incorporated in the lattice during crystal growth. It was proposed that one mode of incorporation of water into the structure of Ag_2CO_3 is for a pair of CO_3^{-2} ions to be replaced by adjacent OH^- and HCO_3^- ions, with two cation vacancies to maintain electrical neutrality. If a cation vacancy lies between the OH^- and HCO_3^- ions, then the ions can hydrogen bond; and, furthermore, if there is sufficient water present so that chains of such centers exist, then the CO_2 can be readily transported via bulk diffusion along the chains of HCO_3^- and OH^- ions.

To provide evidence that might support the model of Barnes and Stone, Gd–Ag_2CO_3 was subjected to chemical analysis for water and infrared analysis. Chemical analysis of Gd–Ag_2CO_3 revealed 1.23 wt % water. The presence of water in Gd–Ag_2CO_3 was not due merely to inadequate drying. Prior to analysis for water and before being used for TGA experiments, the sample was dried over phosphorus pentoxide for 2 months in a darkened dessicator. After that time, pumping on the sample at room temperature (~22°C; background pressure <0.1 torr) for 24 hr did not result in weight loss.

To determine if the reactivity of the doped silver carbonate diminished with prolonged preheating due to a loss of water, a sample was annealed for 5 hr at 100°C in dry nitrogen before increasing the sample temperature at a rate of 5°C/min. Figure 2 shows that the rate of decomposition has not decreased appreciably at comparable temperatures after annealing, as compared to a sample decomposed at a heating rate of 5°C/min without prior annealing. (Since about 22% decomposition occurred while annealing at 100°C, the TGA curve does not begin at $W = 100\%$.)

Table 2 shows the IR bands found with the doped samples and those reported by McDevitt and Baun (*11*) for undoped silver carbonate. Allen and Scaife (*13*) reported splitting of the ν_2 vibration of silver carbonate as was also found with Gd–Ag_2CO_3, Table 2.

IR absorption in addition to that ascribed to CO_3^{2-} was observed at: 682 (m); 837, 848 (m, doublet); 998 (d, shoulder on the 1075-cm^{-1} band of CO_3^{2-}); 2453 (d). All of these bands are in regions of the IR spectrum ascribed by Miller and Wilkins (*14*) to HCO_3^-. Strong, broad absorption using pressed pellets was also observed from 2840

TABLE 2
INFRARED BANDS (cm^{-1}) FOR Gd-DOPED AND UNDOPED SILVER CARBONATE (*11*) THAT ARE ASCRIBED TO CARBONATE SPECIES

Assignment	ν_1	ν_2	ν_3	ν_4	ν_{1+4}
Ag_2CO_3	1072	800, 784	1449	720, 711	1786
Gd–Ag_2CO_3	1075 (d)[a] 1072 (m)	810, 802, 785 (m)	1460 (m)[b]	722, 715 (m)	1788 (d) 1784 (m)

[a] m denotes Nujol mull, d denotes pressed disk.
[b] ν_3 and a Nujol band at 1485 cm^{-1} overlapped (*12*).

to 3635 cm^{-1}. This region of the IR spectrum is characteristic of OH vibration and may indicate the presence of OH^- and/or water of crystallization (*14*). It appears, therefore, that the infrared absorption spectrum of Gd–Ag_2CO_3 is consistent with the presence of some acid carbonate and possibly OH^-, thus providing evidence in support of the Barnes and Stone model.

It was also noted that the Gd–Ag_2CO_3 was more reactive than the most active silver carbonate prepared by Barnes and Stone. This is evidenced by the amount of decomposition (i.e., 22%) that occurred while annealing the doped sample for 5 hr at 100°C in a dry nitrogen atmosphere (see Fig. 2). The most active silver carbonate preparation of Barnes and Stone did not decompose *in vacuo* at 100°C (*10*).

The high reactivity of Gd–Ag_2CO_3 *without water vapor* present might be explained in the following way. Gadolinium 3+ may form a hydrate complex with water, which coprecipitates with silver carbonate during sample preparation thus providing favorable conditions for the Barnes and Stone mechanism to apply. The apparent effect lattice water has on the reactivity of Gd–Ag_2CO_3 suggests lattice water may also have influenced the decomposition kinetics of yttrium-doped silver carbonate (*1*).

The high reactivity of Gd–Ag_2CO_3 cannot be explained on the basis of the low concentrations of reagents used in sample preparation (*10*). The doped samples were prepared at 25°C from 0.1 *M* solutions of silver nitrate containing the appropriate amount of gadolinium nitrate and sodium carbonate.

When decomposition of Gd–Ag_2CO_3 is carried out in the presence of water vapor, the energy of activation, 21.4 kcal/mole, approaches the heat of decomposition for bulk silver carbonate, i.e., 19.2 kcal/mole at 500°K (*15*). This indicates that recarbonation is essentially without energy of activation and that the rate limiting step in the decomposition of Gd–Ag_2CO_3 in a moist atmosphere is resistance to chemical reaction and not diffusion of CO_2 through the layer of reaction product surrounding the carbonate core.

An apparent normal compensation effect is revealed by the kinetic constants in Table 1 and Eqs. (2) and (3), i.e., both the preexponential factor and activation energy decrease with water vapor present (*16*, *17*). (The characteristic temperature, T_s, at which the rate of decomposition is equal in the two cases is 524°K.) The T_s was calculated using the average A and E values, Table 1 and the equation reported elsewhere (*17*).

The apparent compensation effect can arise from either variations in the comparative measurements of decomposition rate versus temperature or from differences in the mechanisms of diffusion and decomposition under the two sets of conditions. The former possibility appears unlikely due to the agreement of the number of independent calculations of E and A, as given in Table 1. The latter possibility as characterized by the simultaneous decrease in both E and A in the presence of water vapor, suggests that the rate-determining step in the decomposition occurs on a smaller number of sites with lower activation energy in this case. Bicarbonate decomposition may occur at a limited surface concentration of bicarbonate–hydroxyl sites in the presence of water vapor, while CO_2 is released primarily by carbonate decomposition at more extensive, but more stable, sites in the absence of water vapor. In either case "linked centers" from constituent water may still provide for lattice diffusion of the CO_2 to the final decomposition site at a gas–solid interface, but the overall decomposition rate may also be affected by the instability of the constituent water sites in the absence of a partial pressure of water vapor.

The isothermal decomposition curves, Fig. 4, show that powder decomposed in either a dry or moist atmosphere and for pellets decomposed in a moist atmosphere, there is no evidence for either an induction or acceleratory period. A similar observation was made using yttrium-doped silver carbonate. The lack of an induction period can be accounted for if lattice defects at surface sites resulting from gadolinium are sites for silver oxide formation. The different crystal structure of Gd–Ag_2CO_3 suggests that the gadolinium does indeed introduce considerable strain in the silver carbonate lattice. Regions of lattice strain on the surface may be sites for silver oxide growth nuclei.

The absence of an acceleratory period could be explained on the basis of rapid two-dimensional growth of the silver oxide nuclei, thus covering the surface of the undecomposed carbonate with a layer of silver oxide. A short induction period was reported for the decomposition of undoped silver carbonate in both the presence and absence of water vapor (*6*, *18*). Since no induction or acceleratory periods were observed, Eqs. (2) and (3) refer to the deceleratory period for the decomposition of Gd–Ag_2CO_3.

In summary, the method of Ozawa was used successfully to obtain the pre-exponential factor, activation energy, and order of reaction from TGA data for the decomposition of Gd–Ag_2CO_3 powder. Water vapor was found to catalyze the decomposition although a normal compensation effect was apparent. However, even in the absence of water vapor, Gd–Ag_2CO_3 was more reactive than undoped silver carbonate preparations studied by others (*10*). This high reactivity may partly be attributed to the significant amount of water incorporated into the crystal lattice during precipitation. Gadolinium probably assists (by complexing) in incorporating water into the silver carbonate lattice. Infrared evidence for OH^- and HCO_3^- in Gd–Ag_2CO_3 has been provided, which aids in supporting the model of Barnes and Stone that was used earlier to explain the variable reactivity of different silver carbonate preparations. The Barnes and Stone model may be used to explain the high reactivity of Gd–Ag_2CO_3 in both the absence and presence of water vapor. Both yttrium- and gadolinium-doped silver carbonate, as well as undoped silver carbonate, obey the interface mechanism for decomposition. Evidence supporting this mechanism is provided by agreement between the experimental decomposition rate in the presence of water vapor and the rate predicted by the Polanyi-Wigner equation. The rate-limiting step in the decomposition of doped and undoped silver carbonate in the presence of water vapor is resistance to chemical reaction and not resistance to mass transfer from the interface through the silver oxide layer.

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