

## Characterization of a Modified Hexagonal Silver Iodide Ice Nucleus Aerosol

PAUL T. SCOTT,\* WILLIAM G. FINNEGAN\*\* AND PETER C. SINCLAIR

*Department of Atmospheric Science, Colorado State University, Fort Collins, Colorado*

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### ABSTRACT

A new ice nucleant aerosol was produced by combustion of a 2% AgI-0.5 mole % BiI<sub>3</sub>-NH<sub>4</sub>I-acetone-water solution. The ice nucleating effectiveness of this aerosol is an order of magnitude greater than AgI alone at -10°C. An X-ray powder analysis identified the aerosol as the hexagonal crystal form of AgI having the closest match to ice ever reported for a nucleant of this type.

### 1. Introduction

An integral part of the design of a weather modification program is the selection of the cloud seeding agent. Solution combustion has long been one of the favored aerosol generation systems and silver iodide (AgI), the favored ice nucleating aerosol. Vonnegut (1949) developed the first solution combustion system for the generation of AgI aerosols. The AgI-ammonium iodide (NH<sub>4</sub>I)-acetone-water solution combustion products were quick-quenched to produce a submicron AgI aerosol. More recently, AgI aerosols have been made with greater effectiveness by attempting to decrease their crystal structural mismatch with the ice structure. Some of these aerosols, e.g., AgI-AgCl, have shown an order of magnitude greater ice nucleating effectiveness than AgI (DeMott et al. 1983). This increased effectiveness could result in a more cost effective program. Combustion generated aerosols other than AgI might also be as cost effective, but none have been developed to the extent of AgI aerosols. This is unfortunate because Fukuta (1958) identified bismuth triiodide (BiI<sub>3</sub>) and lead iodide (PbI<sub>2</sub>) as potential ice nucleants over thirty years ago. Both BiI<sub>3</sub> and PbI<sub>2</sub> were reported to have warmer threshold temperatures than AgI in freezing bulk water. The toxicity of PbI<sub>2</sub> precludes its use as a cloud seeding agent in the United States. On the other hand, bismuth triiodide could be a viable cloud seeding agent if it could be generated in aerosol form.

\* Present affiliation: Environmental Health Lab., Brooks Aerospace Medical Center, Brooks AFB, Texas.

\*\* Present affiliation: Desert Research Institute, Reno, Nevada.

Corresponding author address: Dr. Peter C. Sinclair, Dept. of Atmospheric Science, Colorado State University, Fort Collins, Colorado 80523.

The purpose of this study was to investigate the synergistic interaction of cogenerated BiI<sub>3</sub> and AgI, since both are effective ice nucleants. Synergism is the joint action of agents which when taken together increase each other's effectiveness. By varying ratios of Bi species in the crystalline aerosol to AgI, the ratio giving the best effectiveness was determined. This optimum ratio aerosol was then characterized, isolated, and its crystal structure examined using X-ray diffraction to determine the probable cause for its increased effectiveness. Finally, the data was examined in light of epitaxial and active site theories of AgI heterogeneous nucleation theory.

### 2. Experimental procedures

#### a. Instrumentation and techniques

##### 1) ISOTHERMAL CLOUD CHAMBER

The Colorado State University (CSU) isothermal cloud chamber (ICC) has been previously described by Grant and Steele (1966) and Garvey (1975) and DeMott et al. (1983). The cloud chamber volume is 960 liters. A cloud is produced by continuous atomization of distilled water with a medical ultrasonic nebulizer. After mixing with cold filtered air, the droplets equilibrate to the chamber temperature in a central stand tube. The droplets eventually escape out of the tube at the top of the cloud chamber and slowly settle through the chamber. By varying the rate of droplet introduction, the cloud density is controlled. The density is monitored by a Cambridge dewpoint hygrometer. The liquid water content (LWC) is the difference between the saturation mixing ratio corresponding to the dewpoint temperature and the cloud temperature. The LWC may be varied from 0.3 g m<sup>-3</sup> to 3.0 g m<sup>-3</sup>. The value used for this research was 1.5 ± 0.15 g m<sup>-3</sup>. Temperature is monitored by an array of thermocouples and can be maintained to within 0.2°C.

## 2) TECHNIQUES

The CSU standard test generator was used to produce the aerosols for this study. This generator is basically of the same design as that for field generators and burns atomized AgI-acetone solutions in an auxiliary propane flame. Initial aerosol dilution is accomplished by allowing the combustion products to rise naturally in a vertical wind tunnel (Garvey 1975). The tunnel updraft varies due to outside weather conditions, and care was taken to sample the aerosol only during moderate updraft conditions, e.g. wind < 15 kt. The natural updraft dilution, as measured, was  $1.0 \times 10^5$  L  $\text{min}^{-1}$  at the sampling point (Garvey 1975). After removing a sample with a 4 L syringe, the aerosol was immediately diluted with a known volume of dry ( $-40^\circ\text{C}$  dewpoint temperature) air. This dry dilution prevents overseeding and transient supersaturations on insertion of the aerosol into the ICC. Ice nucleation effectiveness values for a particular aerosol are calculated from the cumulative number of ice crystals falling onto microscope slides as described by Grant and Steele (1966). Effectiveness is defined as the total number of crystals produced per gram of nucleating aerosol at a particular temperature. The rate of reaction and the mechanism of ice crystal formation is determined by a technique described by DeMott et al. (1983). Data are also corrected for cloud chamber airflow dilution of the injected aerosol, when indicated (DeMott et al. 1983).

### b. Materials

The chemical composition of the aerosol from the addition of  $\text{BiI}_3$  to the  $2\text{AgI}\cdot\text{NH}_4\text{I}$ -acetone-water so-

lution combustion system was not determined, but preliminary work indicated the resultant aerosol to be an effective ice nucleant. It was assumed that upon combustion  $\text{BiI}_3$  might not survive intact, but appear as a new chemical species, e.g., bismuth trioxide ( $\text{Bi}_2\text{O}_3$ ) or bismuth oxyiodide ( $\text{BiOI}$ ). Then, upon condensation of the generator flame products, AgI and the resultant form of bismuth would complex to form a solid solution. In order to achieve the most effective aerosol, the quantity of  $\text{BiI}_3$  added to the standard AgI solution was changed by increments dictated by the experiment as the study progressed. Each solution was tested several times, and once the optimum ratio had been established, the procedure was repeated to insure reliability. In addition, the optimum aerosol was tested at different liquid water contents and temperatures. Various aerosol samples representing optimum, excess, and minimal ratios of  $\text{BiI}_3$  were collected on nucleopore filters of  $0.4 \mu\text{m}$  pore size. X-ray powder analyses and identifications of three collected aerosol samples were performed by the Molecular Structure Corporation of College Station, Texas.

## 3. Results and discussion

The aerosols from combustion of various mole ratios of  $\text{BiI}_3$  to AgI in solution were tested at  $-10^\circ\text{C}$  in the ICC to determine each aerosol's effectiveness. Effectiveness plotted against percent mole ratio of  $\text{BiI}_3$  in solution is shown in Fig. 1. Both axes are logarithmic plots for inclusion of all the data. The left and right asymptotes of Fig. 1 represent the average effectiveness of aerosols produced from solutions of AgI (with no  $\text{BiI}_3$ ) and  $\text{BiI}_3$  (with no AgI), respectively. The peak

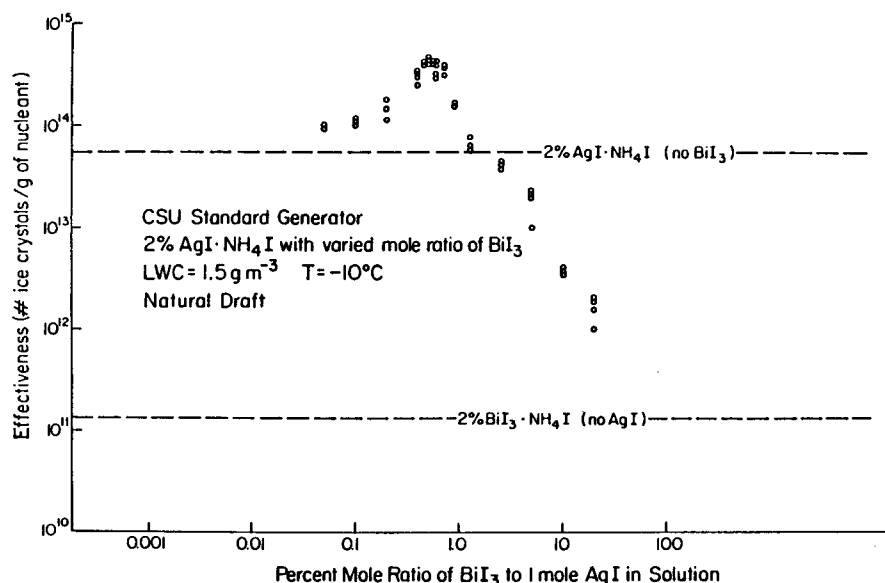


FIG. 1. Effectiveness of nucleation versus varied mole ratios of  $\text{BiI}_3$  to AgI (in solution). Points represent individual experiments.

effectiveness is achieved with the aerosol produced via combustion of the AgI-0.5 mole % BiI<sub>3</sub> (with respect to the AgI) solution. A complete temperature spectrum of the optimum ratio aerosol (AgI-0.5 mole % BiI<sub>3</sub>) is shown in Fig. 2. The average effectiveness at -10°C for this aerosol is  $4.4 \times 10^{14}$  ice crystals per gram of nucleant. When corrected for airflow dilution, the effectiveness at -10° and -20°C is approximately  $8 \times 10^{14}$  and  $2 \times 10^{15}$  ice crystals/g of nucleant respectively. Effectiveness drops off sharply at temperatures warmer than -8°C. From about -8° to -12°C, however, this aerosol has an effectiveness an order of magnitude greater than AgI alone.

Chemical identification of the bismuth species in the aerosol could not be accomplished. Bismuth triiodide is unstable at high temperatures. A BiI<sub>3</sub> (non-AgI) solution on combustion gave an aerosol with minimal ice nucleation effectiveness. Chemical analysis demonstrated that in the absence of AgI, a BiI<sub>3</sub>-acetone solution oxidizes to produce a Bi<sub>2</sub>O<sub>3</sub> aerosol. This result does not suggest however, that Bi<sub>2</sub>O<sub>3</sub> is the species of bismuth incorporated into the resultant aerosol. Any form of bismuth incorporated into the AgI crystal is probably inseparable as an independent molecule or crystal, such as Bi<sub>x</sub>O<sub>y</sub> or Bi<sub>x</sub>O<sub>y</sub>I<sub>z</sub> (O. Anderson, personal communication 1986).

In addition to the characterization of the aerosols for ice nucleus effectivities, the rates and mechanism of ice crystal information were determined. Figure 3 is a kinetic plot of ice crystal formation rates. DeMott et al. (1983) has described the use of chemical kinetics

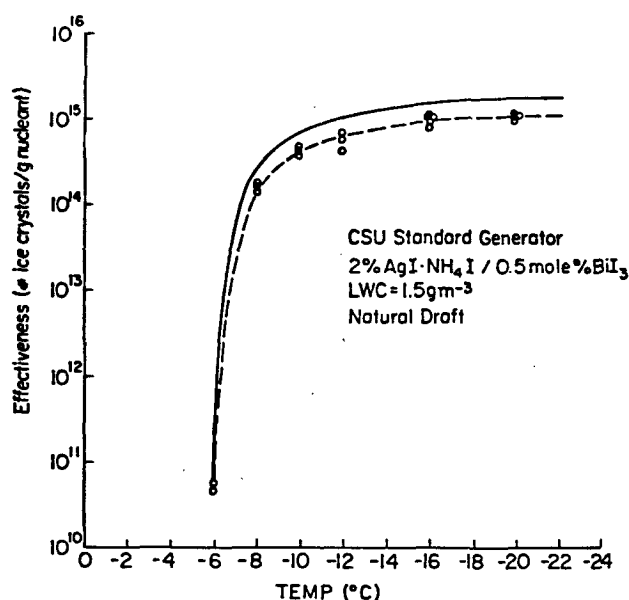


FIG. 3. Kinetic plots of ice crystal formation rates versus cloud chamber liquid water contents.

to determine ice crystal formation rates. In this study, when the cloud liquid water content (LWC), was  $1.5 \text{ gm}^{-3}$ , the ice crystal fallout was 95% complete in 20 min. At  $0.5 \text{ gm}^{-3}$  LWC the fallout was 93% complete by 30 min. There is clearly a different rate constant associated with those experiments run at different LWC and this is indicative of the mechanism of the reaction. If the LWC is changed, the droplet concentration changes and the rate of aerosol-droplet contacts decreases. A nucleant that works via vapor deposition would show a change in rate for a change in water vapor concentration, but not for a change in droplet concentration. Figure 3 therefore implies the optimum ratio aerosol functions at -10°C as a contact freezing ice nucleant.

To identify the aerosol species, three aerosol samples were chosen for X-ray powder pattern analysis. The three samples analyzed were the aerosols from the optimum AgI-BiI<sub>3</sub> 0.5 mole % ratio solution, the AgI-10 mole% BiI<sub>3</sub> solution, and the AgI (no BiI<sub>3</sub>) solution. These aerosols represent the center, right and left extremes of Fig. 1. The X-ray powder pattern analysis identified each aerosol as the hexagonal crystal form of AgI. No other species were identifiable. This was an unusual finding, since previous mixed AgI aerosols (i.e., AgI-AgBr and AgI-AgCl) have been identified as having the face-centered cubic crystal structure (Vonnegut and Chessin 1971; Palinisamy et al. 1986, respectively). The hexagonal form of AgI is stable compared to the face-centered cubic form in the absence of the cubic AgCl and AgBr additives. The hexagonal structure of the modified aerosol is maintained with up to 10 mole % of BiI<sub>3</sub>, suggesting that the Bi species additive does not have or induce the cubic crystal structure.

Though bismuth was not detected by the methods employed, it was incorporated into the aerosol crystal structure. The evidence for the existence of a bismuth species in the aerosol can be seen in the modification of the hexagonal silver iodide lattice. Bismuth addition gives the aerosol (AgI-BiX) a greater ice nucleus effectiveness. These crystal structure modifications can be seen in comparing the lattice constants of the three

FIG. 2. Effectiveness of nucleation versus temperature for the aerosol produced via combustion of the optimum ratio solution of AgI and BiI<sub>3</sub>. The dashed line represents the best fit to the observed data points, and the upper solid line represents the observed data corrected for cloud chamber airflow dilution.

TABLE 1. Compiled x-ray and effectiveness data for three aerosol samples with ice as a reference.

Sample	<i>a</i> axis "a" Lattice constant	<i>c</i> axis "c" Lattice constant	% Disregistry with ice		Effectiveness (ice crystals/g nuclei)
			<i>a</i>	<i>c</i>	
AgI	4.616 ± .002	7.447 ± .006	2.10	2.58	5.6 × 10 <sup>13</sup>
AgI: 0.5 mole % BiI <sub>3</sub>	4.583 ± .002	7.493 ± .006	1.34	1.72	4.4 × 10 <sup>14</sup>
AgI: 10 mole % BiI <sub>3</sub>	4.622 ± .003	7.567 ± .006	2.23	2.72	4.0 × 10 <sup>12</sup>
Ice*	4.521 ± .001	7.367 ± .001	0	0	—

\* From *CRC Handbook of Chemistry and Physics*.

samples (Table 1). Also included in Table 1 is each aerosol's effectiveness and lattice disregistry with ice.

The data show a clear relationship between disregistry and effectiveness. The optimum ratio AgI-BiI<sub>3</sub> solution produced the aerosol with the greatest effectiveness and the closest match to ice. More importantly, the ice disregistry of the optimum ratio aerosol appears to have the closest hexagonal match to ice ever reported. Other aerosols are reported to have a closer match to ice along a single plane, such as the face-centered cubic AgI-AgBr aerosol (Chessin and Vonnegut 1971) and the metaldehyde aerosol (Fukuta 1963), but other mixed AgI aerosols and non-AgI ice nucleating aerosols do not have the hexagonal symmetry which mimics ice.

The reasons for the improved registry with ice on incorporation of bismuth species into the hexagonal AgI crystal lattice are not known. Tripositive bismuth and dinegative oxygen ions have smaller ionic radii than Ag<sup>+</sup> and I<sup>-</sup> ions (1.20Å and 1.40Å compared to 1.26Å and 2.16Å, respectively). Substitution of Bi<sup>3+</sup> and O<sup>2-</sup> for Ag<sup>+</sup> and I<sup>-</sup> would be expected to improve the registry of the aerosol particles with that of ice. Silver bromoiodide and silver chloroiodide both show improved registry by the substitutions of the smaller ionic radii bromide and chloride for the iodide (Vonnegut and Chessin 1971; Palanisamy et al. 1986). Figure 4 proposes a plausible AgI-BiX crystal. The left portion of Fig. 4 shows a model of AgI while the right portion shows the strained AgI with a bismuth substituted for

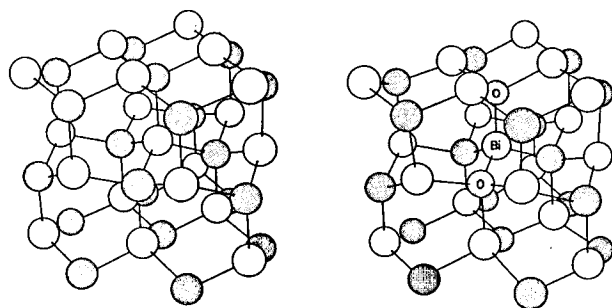


FIG. 4. Proposed crystal structure of the AgI-BiX aerosol (right) with the AgI crystal (left) as a reference. Silver appears as white atoms and iodine as dark atoms. Bismuth and oxygen are as indicated.

one silver and two oxygens substituted for two iodines. The relative size of each crystal may be compared ideally by overlaying the altered structure on top of the AgI structure of Fig. 2. It is hypothesized that this modified AgI crystal, by being a closer match to ice, imposes less strain and hence a lower energy barrier during the epitaxial growth of ice (Turnbull and Vonnegut 1952).

By correlating the data from Table 1 and Fig. 1, the relationship between effectiveness and the lattice disruption can be seen. As the amount of bismuth is decreased from 0.5 mole percent, the effectiveness approaches the effectiveness value of AgI. As the amount of bismuth is increased over the optimum AgI-BiI<sub>3</sub> ratio, it appears that too much bismuth disrupts or strains the AgI crystal and moves the structure away from a match with ice. Much of the credibility for the "closest fit" argument is based on the theory of Turnbull and Vonnegut (1952) which relates an aerosol's disregistry with ice to its threshold temperature of ice nucleation. The effectiveness data do not provide sufficient threshold sensitivity to be related to the minimum temperature of ice nucleation. The AgI-BiX aerosol, however, apparently owes much of its ice nucleation ability to its close match with ice. Despite this, the possibility remains that the inclusion of foreign elements into the AgI crystal surface and lattice provides active sites which can serve as nucleation centers. The physical and chemical properties of the AgI particle surfaces have been changed by the addition of the bismuth species.

#### 4. Summary

One of the original aims of this research was to show a synergistic relationship between two ice nucleating aerosols. While the effectiveness of the resultant aerosol, AgI-BiX, is greater than the effectiveness of AgI or Bi<sub>2</sub>O<sub>3</sub>, the synergistic relationship obtained was not quite as initially expected. The optimized molar ratio of BiI<sub>3</sub> to AgI in solution was determined to be 0.5:99.5. The effectiveness of the combustion aerosol was an order of magnitude greater than that for an AgI aerosol and its mechanism of ice crystal formation was freezing nucleation by contact. Bismuth triiodide in acetone solution was transformed upon combustion to

form a  $\text{Bi}_2\text{O}_3$  aerosol which was ineffective as an ice nucleant. The dramatic rise in effectiveness as the addition of  $\text{BiI}_3$  to  $\text{AgI}$  approached 0.5 mole % from either direction (Fig. 1) prompted an investigation into the reason for this behavior. Previous work with  $\text{AgI}$  has shown the stable nature of the hexagonal crystal form of  $\text{AgI}$  and its modification to the face-centered cubic form on addition of  $\text{AgCl}$  or  $\text{AgBr}$ . The X-ray powder pattern analysis of collected aerosols indicated the hexagonal crystal structure for the  $\text{AgI-BiX}$  aerosol even when the  $\text{BiI}_3$  to  $\text{AgI}$  was as large as 10 mole %. The relationship between crystal structure dimensions and ice nucleus effectiveness is quite apparent. The "a" and "c" axis ice disregistry showed that the  $\text{AgI-BiX}$  aerosol produced (via combustion of a 2%  $\text{AgI-0.5}$  mole %  $\text{BiI}_3\text{-NH}_4\text{I-acetone-water}$  solution) had the closest hexagonal match to ice reported thus far in the literature. The bismuth species role in the hexagonal  $\text{AgI}$  crystal structure is hypothesized to create a "lattice disruption". In shrinking the  $\text{AgI}$  crystal, the larger ionic radii of silver and iodide are substituted by the smaller ionic radii of bismuth and oxygen. Thus less strain is encountered in the epitaxial growth of ice.

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