AN EFFICIENT, FAST FUNCTIONING NUCLEATING AGENT -- AgI·AgCl-4NaCl[1]

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Abstract. A composite ice nucleus aerosol, AgICl-4NaCl, has been generated and characterized for nucleation efficiencies, rates of ice crystal formation, and mechanisms of nucleation, under water saturation and transient supersaturation conditions. The addition of NaCl to the highly efficient contact nucleus, $AgI_{0.8}Cl_{0.2}$, changed the nucleation mechanism to condensation-freezing at water saturation and increased the rates of ice crystal formation dramatically, while retaining the high efficiency of the AgICl nucleus aerosol. Under transient supersaturation conditions, this new aerosol demonstrated improved ice nucleation efficiencies at T > -12 C, and even faster ice crystal formation rates, suggesting a change of nucleation mechanism to forced condensation-freezing. This ice nucleation aerosol should be advantageous for use in weather modification field programs under conditions where low cloud droplet concentrations suggest the use of a condensation-freezing nucleant.

1. INTRODUCTION

Since Vonnegut found in 1947, that silver iodide aerosols are effective ice nuclei, AgI has been widely used in weather modification experiments and operations as cold-cloud nucleating agents. When generating AgI, other chemical substances are usually added. For example, when using AgI-acetone solution combustion as a generating method, NH_4I, KI or NaI is added as a solubilizer. In AgI pyrotechnics silver iodate $AgIO_3$ is used as an oxidizer, and magnesium, and aluminum as fuels. Even though AgI artificial ice nuclei can be generated by many different ways, they are not pure AgI aerosols because of the existence of other chemical materials. Due to the different properties of the added materials, the ice nucleation mechanisms, the nucleation efficiencies and the nucleation rates will therefore be different.

Vonnegut and Chessin (1971) compared the nucleation efficiencies of pure AgI and AgI·AgBr. Their results showed that pure AgI has a lower nucleation efficiency. They also found that the lattice structure will be closer to that of ice if part of the iodine atoms are replaced by bromine atoms. Sax, et al., (1979) found that some of the Nuclei Engineering, Inc. (NEI) pyrotechnic formulations contained small amounts of chlorine and had aerosol nucleation efficiencies at -10 C, which were one or two orders of magnitude higher than those which did not contain chlorine. They concluded that this increase was caused by the chlorine changing the lattice structure, or introducing active sites on the AgI surface. Later DeMott, et al., (1983) generated AgI·AgCl compound nuclei using an AgI-NH_4I-NH_4ClO_4-acetone-water burning system. Such nuclei have one order of magnitude higher nucleation efficiencies at -12 C and three orders of magnitude higher efficiency at -6 C than that of pure AgI produced by the AgI-NH_4I-acetone system. They also showed that both of these nuclei are contact nuclei, and the nucleation rates are relatively slow. Blumenstein, et al., (1983) showed that the 2AgI-NaI nucleus aerosol is strongly hygroscopic and nucleates by a condensation-freezing nucleation mechanism. Under water-saturation condition, the nucleation rate is very slow and the nucleation efficiency is also low. Under transient supersaturation conditions there is a clear increase of nucleation rate, and the nucleation efficiency also increases at warmer temperatures. Feng and Finnegan (in preparation) studied the T8-1 pyrotechnic aerosols manufactured by different suppliers and concluded that there are big differences in the nucleation mechanisms using the same combination of substances. The pyrotechnics made by the U.S. Navy gave aerosols with lower nucleation efficiencies, but with very high nucleation rates and which were clearly acting as condensation-freezing nuclei. The aerosols from the pyrotechnics made by NEI have a lower nucleation rate and were reacting as contact nuclei. One possible reason is that the materials of different pyrotechnic formulations have different impurities. Therefore, the composition of AgI and different chemical impurities will lead to different nucleation mechanisms, different effectivenesses, and different nucleation rates.

Among various artificial nuclei, AgI·AgCl nuclei have the highest nucleation efficiencies (DeMott, et al., 1983), but they are contact nuclei with low nucleation rates. If hygroscopic material is added, it was thought possible that the nucleation mechanisms would be changed to

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condensation-freezing. With a careful choice of hygroscopic material, the advantage of the high nucleation efficiency could be retained, and a new high nucleation rate aerosol obtained.

2. INSTRUMENTATION AND PROCEDURES

The experiments were conducted in the isothermal cloud chamber of the Department of Atmospheric Sciences, Colorado State University. The cloud produced by the ultrasonic fog generator, was cooled to the chamber temperature before introduction into the chamber. The sizes of the cloud droplets are between 1-16 microns with mean diameter of 7 microns. The liquid water content inside the chamber was maintained at a constant value for each experiment. The values of liquid water content usually chosen were 0.5 g m^{-3} (with corresponding droplet concentration of 2100 cm^{-3}) and 1.5 g m^{-3} (4300 droplets cm^{-3}). The temperatures at different points of the chamber could be controlled with an accuracy of +- 0.3 C. The aerosols produced by the generator were diluted with ambient air in the wind tunnel. A volume of 4 liters of such diluted air was taken by a sampling syringe then mixed, at fixed ratios, with either pure dry air or saturated air at room temperature. The diluted aerosol samples were then injected into the cloud chamber. The ice crystals produced by the aerosols, fell onto pre-cooled microscope slides. The slides were taken out at certain time intervals (1-3 min.) and the number of ice crystals on the slides counted using a microscope. This process continued until the ice crystal generation ceased. From the cumulative number of ice crystals obtained from each experiment, the nucleation efficiency was calculated. The ice crystal nucleation rate was obtained by counting the number of ice crystals as a function of time. Detailed information about this chamber can be found in Garvey (1975).

In the past, this chamber was used to compare the nucleation efficiencies for various nucleant aerosols and those from different types of generators (DeMott, et al, 1983). In recent years, in cloud simulations and aerosol experiments, the method of chemical kinetics was introduced into the isothermal cloud chamber experiments (DeMott, et al., 1983). By observing the ice crystal nucleation rates changing with time after the aerosols had been introduced into the chamber, the nucleation rate and its relationships with various parameters (such as temperature, droplet concentration, supersaturation ratio, etc.) of the chamber, can be studied and the nucleation mechanisms can be determined. In this way, the nucleation characteristics of various artificial aerosols can be studied. The same methods were used in this experiment.

This experiment was based on the basic composition of AgI·AgCl studied by DeMott, et al., (1983). Sodium chloride (NaCl) was used as the hygroscopic material to add to AgI·AgCl. The reason for this choice is that NaCl will neither form complex compounds nor produce solid solutions with AgI. This addition was achieved by adding sodium perchlorate ($NaClO_4$) to the original solution, e.g., AgI-NH_4I-NH_4ClO_4-$NaClO_4$-H_2O-acetone. Sodium perchlorate is easily soluble in acetone (50 g $NaClO_4$ / 100 g acetone), and is reduced to NaCl during solution combustion. The AgI·AgCl-NaCl aerosols then result from combustion of the total solution.

There were two parts to this experiment. First, the temperature in the chamber was maintained at -10 C while changing the molar ratio between AgI and $NaClO_4$ in the solution in order to determine the optimum composition of AgI and NaCl in the generated aerosol. Secondly, the nucleation efficiencies and rates of this optimum composition were determined between -5 and -20 C.

3. EXPERIMENTAL RESULTS

3.1 The Best Molar Ratio of AgI to NaCl

In the testing solution, the molar ratio of AgI to $NaClO_4$ was changed from 1:0.5 to 1:5. The aerosols produced by combustion were diluted with dry air or saturated air at room temperature, and were then injected into the chamber at -10 C. In each, the nucleation efficiency was calculated from the total number of ice crystals produced, the rate of formation of AgI and the dilution ratio. The nucleation rate can be expressed in different ways. In this study, the time that 90% of the ice crystals formed (T90), is used as the nucleation rate. Figure 1a shows the AgI nucleation efficiency at different $NaClO_4$ molar concentrations. Figure 1b shows T90 as a function of the $NaClO_4$ concentration. The values for pure AgI in these figures were obtained from the results of DeMott, et al., (1983).

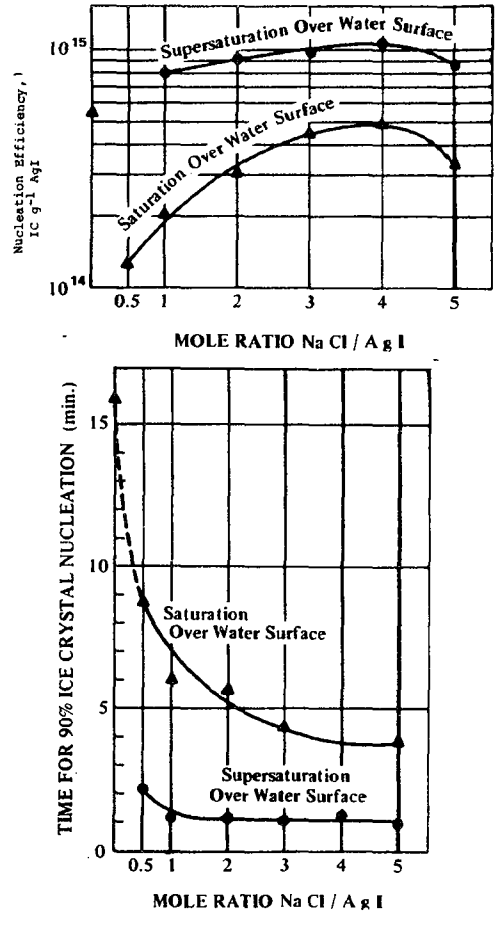

Fig. 1 Nucleation efficiencies (a) and times for 90% ice crystal nucleation (b) as a function of the NaCl/AgI ratios at -10 C.

Figure 1 shows that the highest nucleation efficiency and rate occur when the molar ratio between AgI and $NaClO_4$ was 1:4. At water saturation, the nucleation efficiency reached 4.9 x 10^{14} g^{-1} AgI at -10 C, which was very close to the nucleation efficiency of AgI·AgCl, (5.4 x 10^{14} g^{-1} AgI), under the same conditions. T90 was 3.8 min. for the composite nuclei, but for AgI·AgCl aerosols T90 was 16 min. When the sample was diluted with saturated air at room temperature, and injected into the chamber, a transient supersaturation was induced in the chamber. The nucleation efficiency reached 10^{15} g^{-1} AgI at a molar ratio of 1:4. The nucleation rate increased dramatically with T90 shortening to 1.2 min.

3.2 The Nucleation Efficiency and Nucleation Rate as Functions of Temperature

Aerosols produced by burning the solution with the optimum molar ratio of AgI to $NaClO_4$ at -10 C were tested in the temperature range between -5 C and -20 C. Two sets of results were obtained under both water-saturation and transient supersaturation conditions. These results are shown in Figure 2.

Over the whole temperature range, the AgI·AgCl-4NaCl composite nuclei had very high nucleation efficiencies at water saturation, and they were close to the nucleation efficiency of the AgI·AgCl nuclei. The nucleation efficiency increased dramatically from -5 C to -12 C and reached 2 x 10^{15} g^{-1} AgI at -12 C. As the temperature was decreased further to -20 C, the efficiency increase was slight with only a small increase under transient supersaturated conditions. The nucleation efficiency was lower than the values obtained at water-saturation in the temperature range between -5 and -7 C, but it is higher than those for water saturation values between -7 C and -20 C with the largest difference of about a half order of magnitude (see Figure 2a).

The nucleation rate increased with decreasing temperature. At water saturation, T90 was 18 min at -6 C and 1 min at -20 C. The change in nucleation rate with temperature was large when T > -12 C. In the -6 C to -12 C range the nucleation rate, under transient supersaturation conditions, increased much faster than under water-saturation conditions. T90 decreases from 18 min to 2 min at -6 C, but in the lower temperature range (-14 C to -20 C) there was no great difference between the supersaturation and water saturation values (Figure 2b).

3.3 The Nucleation Mechanism

In order to study the changes in the nucleation rate with changes in the concentration of droplets, we performed experiments with liquid water contents of both 0.5 g m^{-3} and 1.5 g m^{-3} at two different temperatures, -8 C and -20 C. The results are shown in Figure 3. The nucleation rate of the composite nuclei does not change with the liquid water content (or the droplet concentration). Therefore, AgI·AgCl-4NaCl nuclei are not contact nuclei. It is shown, from the experiments at both water saturation and supersaturation conditions, that these nuclei are sensitive to water vapor density, and both the nucleation efficiency and the nucleation rates increase greatly under transient supersaturation conditions. These results show that the nuclei are condensation-freezing nuclei.

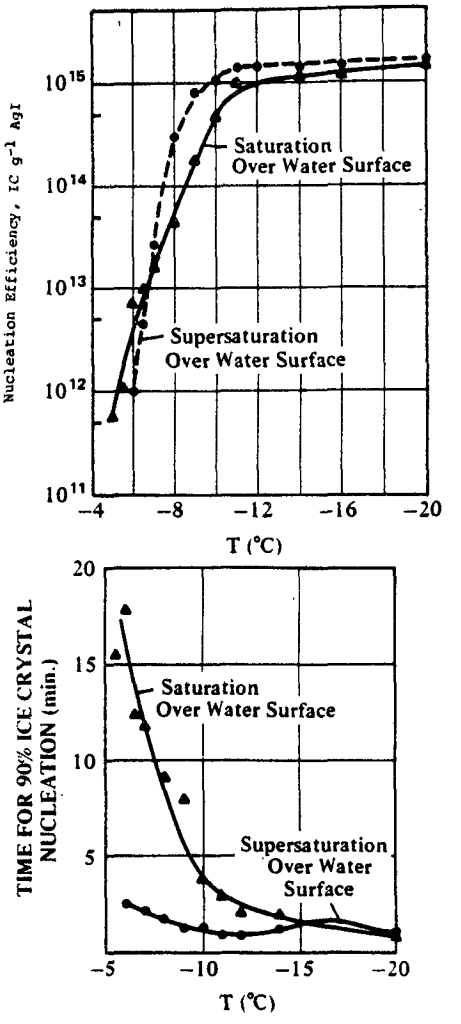

Fig. 2 Nucleation efficiencies (a) and times for 90% ice crystal nucleation (b) of AgI.AgCl-4 NaCl composite nuclei as functions of temperature and humidity.

3.4 Comparison with Other Nuclei

There are many other artificial nuclei generated by acetone solution combustion which have been used for weather modification purposes, but the most popular ones in recent years are AgI, AgI·AgCl, and 2AgI·NaI. The same kinds of studies were then conducted with these three nuclei as with our composite nuclei. Comparison between them are as follows. Some results on AgI and AgI·AgCl nucleus aerosols were obtained from DeMott (1982), and the results on 2AgI·NaI were from Blumenstein, et al., (1983). Their nucleation efficiencies and nucleation rates at -10 C are shown in Figure 4a and 4b, respectively. Figure 4a shows that the nucleation efficiencies of AgI·AgCl-4NaCl and AgI·AgCl nuclei are quite similar. The largest difference occurs at -8 C with AgI·AgCl nuclei two-fold higher than AgI·AgCl-4NaCl. At this time, AgI·AgCl nuclei have the highest nucleation efficiency of all artificial nuclei. This conclusion was drawn from

laboratory experiments where high droplet concentration can promote more rapid contact nucleation of AgI·AgCl nuclei to achieve the higher nucleation efficiencies and rates. In the real atmosphere, the concentration of supercooled droplets is about one order of magnitude smaller than that in the chamber, resulting in much slower nucleation rates for contact nuclei.

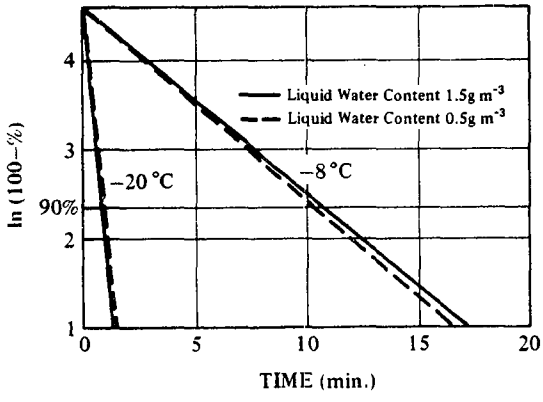

Fig. 3 Rates of depletion of AgI.AgCl-4 NaCl composite nuclei after introduction into the cloud chamber at different liquid water contents.

The AgI·AgCl-4NaCl nuclei are condensation-freezing nuclei, and will retain their nucleation rates, as measured in the chamber, because the nucleation mechanism is independent of droplet concentration. The comparison of AgI·AgCl-4NaCl nuclei with the pure AgI nuclei from AgI-NH_4I-acetone solutions shows that the nucleation efficiency of the composite nuclei is one order of magnitude higher at T > -12 C. The nucleation efficiency of AgI·AgCl-4NaCl nuclei was 2-3 orders higher than that of 2AgI·NaI nuclei, and the differences decrease with decreasing temperature. Figure 4b shows that after AgI·AgCl-4NaCl nuclei were injected into the chamber at -10 C, ice crystals were quickly produced, and the production rate decreased rapidly. The nucleation rate of the AgI·AgCl-4NaCl composite nuclei is faster than those measured for the other three kinds of nuclei.

4. CONCLUSIONS

As expected, if the hygroscopic material, NaCl, is added to AgI·AgCl aerosols, the nucleation process changes from contact nucleation to condensation-freezing nucleation. These experiments gave the optimum molar ratio of AgI·AgCl to NaCl and resulted in the fast and more efficient composite nuclei, AgI·AgCl-4NaCl. The discovery of these composite nuclei is important in the seeding of cumulus clouds with very strong updrafts and orogaphic clouds with strong horizontal wind speeds, in which high concentrations of ice crystals need to be generated in relatively short time periods. This factor is also important in cold fog dispersion operations.

In these experiments, only the optimum molar ratio of NaCl to AgI·AgCl for maximum efficiencies and rates was determined. Information on the size distributions of the aerosols generated and their chemical components still need further research and analysis. More research is needed on whether the nucleation mechanism of these composite nuclei will change if these nuclei are injected into the lower warm (T > 0 C) parts of clouds before they reach the upper cold (T < 0 C) regions. More experiments are needed on how to generate these kinds of composite nuclei, such as pyrotechnic generation.

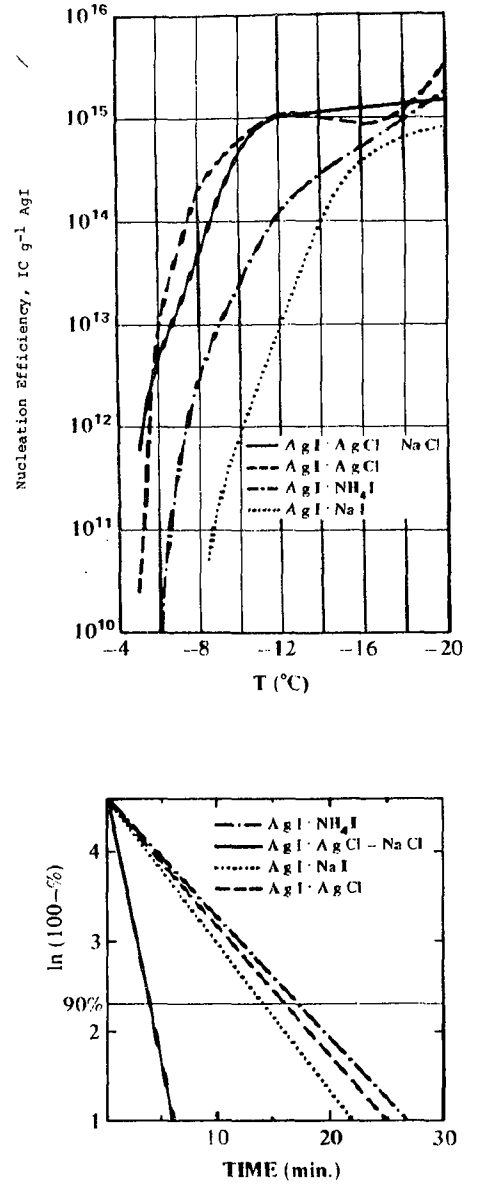

Fig. 4 Comparison of nucleation efficiencies (a) and rates of depletion of nuclei after introduction into the cloud chamber (b) for several different aerosols.

5. ACKNOWLEDGEMENTS

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