Freezing of Water Droplets: Nucleation Efficiency at Temperatures above -5°C

F. KIRK ODENCRANTZ

Naval Weapons Center, China Lake, Calif.

(Manuscript received 26 September 1968, in revised form 24 January 1969)

ABSTRACT

Numerical values obtained in laboratory studies of nucleation effectiveness of pyrotechnically produced smokes are strongly dependent on experimental conditions. Contact nucleation is shown to be relatively important at warm temperatures, when the nuclei are produced in a supercooled cloud of high liquid water content. Thus, pyrotechnics designed to produce nuclei in supercooled clouds should be tested under appropriate conditions.

1. Introduction

The ability of a particle to serve as an ice nucleus is dependent on its present and past environment. Nucleating material may be dispensed external to the cloud with the hope that a significant portion may eventually be carried into the cloud, or it may be dispensed directly into the cloud. The choice of the method of measurement of nucleation efficiency of a material should be dictated by the conditions the nucleus is expected to encounter prior to fulfilling its role as a nucleant.

Ice nucleation in the atmosphere may be the result of several competing processes. Water vapor may sublime on the nucleating material. It may condense on the nucleus and be followed by the freezing of the condensed water film. Or, the nuclei may contact a supercooled water drop and, while on the surface or after entering the drop, induce freezing. The concentration of both the droplets and the nucleating particles, the temperature and size of the drops, as well as the characteristics of the nucleating material determine which of the processes is the most important. The nucleation efficiency, as measured in the laboratory, is strongly dependent on the experimental conditions. It depends on the liquid water content, the distribution of droplet sizes, the presence of contaminant vapor such as ethylene glycol, and the concentration and history of the nuclei. Thus, it does not appear practical, at present, to isolate the nucleation processes and determine the kinetics of the individual processes for all of the many nucleating agents that have been and are being developed. However, it is reasonable to approximate, as closely as possible in the laboratory, the environment to which nuclei will be subjected in an actual field operation.

2. Experimental technique

The pyrotechnic materials designed for nuclei generation in supercooled clouds are tested at NWC by

burning a small quantity of the pyrotechnic in a supercooled cloud in a 24-m^3 cold chamber. The supercooled cloud is produced by injecting steam into the bottom of the chamber. The fog that is produced is allowed to come to equilibrium with the air and the walls of the chamber before it is seeded. The initial liquid water content of the air is $\sim 3\text{ gm m}^{-3}$. The ice crystals that are formed and grow large enough to fall on a Formvar-coated slide near the floor of the chamber are replicated with chloroform vapor. The replicated crystals

FIG. 1. Nucleation efficiency vs temperature for a pyrotechnic containing various amounts of AgIO_3 and $\text{AgIO}_3 + \text{KIO}_3$.

are assumed to be a representative sample and the density on the slide is determined by counting with a microscope.

It should be noted that the nucleation efficiencies obtained by this method will differ from the values obtained by investigators using different measurement techniques. This technique would not be expected to give a good representation for cases where the seeding agent is produced on the ground and the aerosol is airborne to the cloud, or where the agent is initially produced in a warm ($T > 0^\circ\text{C}$) cloud since the effectiveness of nuclei is dependent on their environmental history. A high water content cloud is seeded under essentially static conditions in the NWC chamber. It is difficult to monitor (as well as to maintain) uniform conditions in the chamber if a low water content cloud is heavily seeded and sufficient water is added to try to maintain a constant quantity of water vapor. The number of effective nuclei produced in the chamber is a linear function of the quantity of pyrotechnic burned, provided less than 10^{10} ice crystals are produced. Normally, the sample size is selected so that less than 3×10^9 ice crystals are produced. At cold temperatures ($< -12^\circ\text{C}$) the pyrotechnic smoke often saturates the chamber with nuclei. Consequently, the results below this temperature represent only a lower limit of the nucleation efficiency. A procedure to mix AgIO_3 with an "inert" material in the pyrotechnic to extend the measurements of the activity to lower temperatures has been discontinued. The dilution of the AgIO_3 with

FIG. 2. Nucleation efficiency vs temperature for two pyrotechnic materials developed for seeding by dispensing the smoke in supercooled clouds.

FIG. 3. A "shell" frozen drop illustrating a well developed spicule.

"inert" materials may so modify the nature of the nucleant that such a technique cannot be used to extend the range of measurements to lower temperatures. The lack of linearity of nucleation efficiency vs AgIO_3 concentration is evident in Fig. 1. The nucleation efficiency-temperature dependence of pyrotechnics containing various quantities of AgIO_3 and also $\text{AgIO}_3 + \text{KIO}_3$ is dependent on the AgIO_3 concentration and other parameters.

The present techniques are useful, however, since the region of interest for the production of precipitation by artificial nuclei is primarily in the region warmer than -12°C .

Effects of the addition of alkali iodates to silver iodate pyrotechnics have been reported by Finnegan *et al.* (1967). The addition of a moderate quantity of alkali iodate (with the exception of CsIO_3) to the AgIO_3 pyrotechnic increased the nucleation efficiency in the temperature region between -10 and -5°C . It has been suggested¹ that the soluble alkali-iodide/silver-iodide complex dissolved in sufficient water to cause the AgI to precipitate out of solution. The AgI would then serve as a freezing nucleus for the supercooled water.

In experiments performed as early as 1965, it was noted that smoke from an AgIO_3 pyrotechnic was able to induce freezing of supercooled water drops at temperatures as high as -1°C . This is considerably warmer than the generally reported nucleation threshold for AgI . Later investigations revealed that the AgIO_3 may have contained up to 3% KIO_3 . The presence of other alkali compounds in the pyrotechnics may also have contributed to the observed effect.

The difference between nucleation efficiency curves for two pyrotechnic materials developed for seeding by

¹ Burkardt, L. A., W. G. Finnegan and F. K. Odencrantz. Compositional effects on ice nuclei activity. Paper presented at the 48th Annual Meeting, Amer. Meteor. Soc., 29 January-1 February 1968, San Francisco, Calif.

FIG. 4. A thin section of a "shell" frozen drop viewed between crossed polarizers.

dispensing the smoke in supercooled clouds (Fig. 2) is pronounced at warm temperatures. The effect of the KI in the smoke may be to induce water condensation on the smoke particles, or KI may be complexed with AgI to produce a smoke particle that could dissolve in any droplet it might contact. Experiments on large water drops with less than 5°C supercooling indicated that the freezing could depend on the nucleation.

Experiments on large drops were performed in the following manner. Sets of 50 distilled water drops, measuring 3–4 mm in diameter, were placed on Teflon sheets. Each sheet, with 50 drops, was placed in a separate Plexiglas box and three sets were cooled simultaneously for several hours in the cold chamber. The temperature of the air in the Plexiglas boxes was maintained at the desired level for at least 30 min prior to admission of the nucleating material. The Teflon sheets were rewashed and the experiment was repeated if nucleation from contamination was evident prior to seeding. The smoke from the combustion of approximately 25 mg of AgIO_3 pyrotechnic was then added to the 3-liter Plexiglas box. The droplets that were unfrozen after 15 min were recorded as unfrozen.

Drops nucleated on the surface tended to form an ice shell which, as the heat of fusion was conducted away from the ice-water interface, moved toward the center of the drop, pushing the air (precipitated out of the water as it froze) ahead of the freezing front and compressing the unfrozen water. This pressure builds up until the shell either ruptures explosively or cracks and allows a portion of the air and water to escape (Hobbs and Alkezweeny, 1968; Mason and Maybank, 1960). A photograph of a typical drop with a frozen spicule is shown in Fig. 3, while a photomicrograph of a thin section of a horizontally sliced "shell frozen" drop between crossed polarizers is seen in Fig. 4. This drop was supercooled and then seeded by allowing ice crystals

TABLE 1. Nucleation of distilled water droplets (initial temperature -2.0°C).

Seeding agent	Number frozen	Number with spicules	Number shattered
AgIO_3 pyrotechnic smoke	16	0	0
$\text{AgIO}_3 + \text{KIO}_3$ pyrotechnic smoke	46	2	0
Ice crystals (airborne)	47	28	5

from a dense ice fog to settle on the drop. It indicates that the supercooled drop was effectively seeded at several positions on its surface. Occasionally, examples of frozen drops consisting of a single crystal have been observed.

When freezing is initiated from the interior of a supercooled drop, parallel plate-shaped dendrites of ice rapidly grow throughout the drop. The density of the dendrites depends on the initial supercooling of the water and the rate of conductivity of heat from the droplet (Rohatgi and Adams, 1967). Further freezing proceeds as the heat of fusion is dissipated to the atmosphere. Since air is less soluble in ice than water, it collects in the channels with the residual water as it is driven from solution by the freezing. Finally, the rows of tiny air bubbles remain as evidence of the last frozen regions of the drop. If a supercooled drop is seeded by contact of a splinter of ice large enough that the drop wets the ice, dendritic platelets grow rapidly through the drop. A thin section of a dendritic frozen drop is shown in Fig. 5.

If the surface tension of the water is decreased with the addition of a small quantity of surface active material, and small ice crystals are allowed to fall on the supercooled drops, the freezing appears to start as a shell type of growth. However, this condition does not persist, and in a very short time the dendritic type of

FIG. 5. A thin section of a "dendritic" frozen drop viewed between crossed polarizers. The rows of air bubbles are characteristic of this type of freezing.

growth appears. This latter type of growth progresses far more rapidly, so that once it starts, it becomes and remains dominant in its influence on the final state of crystallization.

Metaldehyde particles are effective in nucleating the surface of supercooled water drops. In an experiment at -4.5°C , metaldehyde, vaporized from a small metal dish on the tip of a soldering gun, sublimed in the air to form seeding nuclei. This seeding produced 28 drops with definite spicules, 3 shattered drops, and various degrees of protuberance on the remainder of the 50 drops. A companion set of drops, seeded with AgIO_3 pyrotechnic smoke, produced no spicules or shattering from a set of 50 drops.

FIG. 6. Number of drops frozen from a set of 50 supercooled drops within 15 min of exposure to pyrotechnic smoke.

The results of one experiment on the nucleation and freezing of three sets of supercooled drops are illustrated in Table 1.

Results of similar experiments are summarized in Fig. 6. Thin sections of frozen drops nucleated with $\text{AgIO}_3\text{-KIO}_3$ pyrotechnic smokes show dendritic crystal growth. These droplets were probably nucleated after contact with smoke particles. Contamination of the drop or solution of a soluble portion of the smoke (such as AgI-KI) followed by the precipitation of AgI in the interior of the droplet may account for the observed dendritic growth.

The role of contamination on nucleation and freezing is not understood. The effectiveness of a nucleating agent may be modified by traces of impurities in the nucleant or by contamination in the atmosphere (Odenclantz, 1968). The existence of a relationship between the nucleating agent and the freezing mechanism is indicated for 3-4 mm diameter supercooled water drops seeded by contact with the nuclei. It is suggested that contact nucleation is responsible for the apparent extension of the " AgI " nucleation threshold to warmer temperature. Consequently, this mechanism should be considered in the evaluation of nucleation materials that are initially dispersed in supercooled clouds.

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