ON THE FORMATION OF ICE UNDER THE INFLUENCE OF PbI_2 PARTICLES.

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INTRODUCTION

Lead iodide introduced into a supercooled cloud can act according to two different machanisms: through contact of the nucleating ice particle with a supercooled drop or through ice growth at a suitable site on a nucleating particle.

A third possibility - the freezing of a supercooled drop by direct interaction between the water and a particle completely immersed in it must be excluded because of the relatively higher solubility of lead iodide in water.

In this paper some possibility of ice formation on PbI_2 particles are studied.

METHOD

The following criterion was chosen to demonstrate the existence of ice on a single particle of the nucleating agent. The ability of a particle to initiate freezing when brought into contact with a supercooled water droplet (down to several tenths of a degree centigrade) was taken as proof of the existence of ice on the particle surface.

Experiments were carried out in a small chamber (15 cm^3 in volume) cooled with liquid nitrogen. The chamber was in the shape of a vertical cylindrical hole 16 mm in diameter drilled in brass block. Eight mutually connected channels were bored in the walls of the block. Liquid nitrogen dosed periodically into the channels evaporates and cools the brass block. The bottom of the chamber was closed with a stopper, whereas the top was equipped with a holder for a thermocouple. The thermocouple was melted into a thin-wall glass capillary.

The chamber had another four holes placed symmetrically in the horizontal plane so that their optical axes were mutually perpendicular and intersected each other in the geometrical center of the chamber. A water droplet suspended on the tip of the thermocouple was placed in the center of the chamber through the upper opening. Two of the horizontal holes permitted illumination and observation of the droplet in mutually perpendicular directions. The cooling system was automated and a suitable cooling rate could be chosen. In addition, an alternative heating system facilitated temperature control of the chamber.

PROCEDURE

A drop of distilled water was suspended on the glass capillary covering the thermocouple and placed in the chamber. A fine glass filament carrying a small amount of PbI_2 powder on its rounded tip was introduced through one of the horizontal holes. This filament was attached to a micromanipulator by means of which the filament could be brought into contact with the water drop. At the beginning of an experiment the tip of the filament was kept 2-3 mm away from the drop surface. To allow for a thermal gradient in the chamber another thermocouple without a glass cover was inserted through another horizontal hole and placed in the same distance from the drop surface. Due to its symmetrical position in relation to the position of the PbI_2 position this thermocouple indicated with sufficient accuracy the temperature of the PbI_2 particles in the chamber. The signal from either of the thermocouples can be selected by a commutator and registered by a recorder.

In the first stage of the experiment, the temperature in the chamber was decreased slowly down to the value T_0 measured by the thermocouple inserted through the horizontal hole. The drop does not freeze during this cooling process. Then the temperature in the chamber was slowly increased to the value T_s which was close to 0^oC but always below the freezing point, usually in the range from -0.5^oC to -1.5^oC. The small temperature difference between the two thermocouples in the chamber disappeared during the slow increase in temperature. The PbI_2 particles at the glass filament tip were brought into contact with the drop by means of the micromanipulator while the response of the thermocouple carrying the drop was recorded. Freezing of the supercooled drop kept at a temperature slightly below zero indicated the existence of ice on the PbI_2 particles. Several experiments were carried out according to the above procedure with clean glass filaments after removal of all adhering PbI_2 particles, to show that ice was not formed on the glass surface. This was, in fact, confirmed by a series of experiments in which the temperature of the filament tip reached -10^oC but subsequent contact with the drop did not initiate freezing.

RESULTS AND DISCUSSION

Table 1 gives the experimental conditions for 20 experiments, carried out according to the described procedure. Analyses of the experimental data in table 1 proved that the droplet temperature at the moment of a contact (always close to 0^oC) had no influence on whether the droplet froze or not. The only condition that must be fulfilled is that T_s is $< 0^oC$. The last two columns in table 1 give mean values of T_0 and T_s in experiments when droplets had frozen and when had not; however, exact physical meaning cannot be associated with these values. It is obvious that the mean temperature T_0, of previous cooling was considerably lower (-5.8^oC) in cases when the droplet had frozen than when freezing was not observed (-3.8^oC), while the mean temperature during contact was almost the same in the two groups of experiments. For better characterization of this phenomenon, 90 experiments were performed according to the described procedure varying only the temperature of the preliminary cooling of the PbI_2 particles. Table 2 gives the relative frequencies of the cases in which freezing occured related to the temperatures of the preceeding cooling expressed for temperature intervals of 1^oC. After the previous cooling of the PbI_2 particles to a temperature from -3.1^oC to -4.0^oC, freezing of droplet occurred on contact in one third of all cases (the first column in table 2); with cooling temperatures ranging from -4.1^oC to -5.0^oC, ice was formed in two-thirds of all experiments; after cooling below -6.0^oC, freezing was invariably observed in all experiments. The relative frequency values in the second column of table 2 were calculated for temperature intervals of 1.0^oC excluding cases in which freezing occurred at lower temperatures than those cited. The median temperature of precious cooling leading to the freezing of droplets was -4.7^oC, as follows from the data in table 2.

Further, the affect of elevated temperatures on the ice-nucleating properties of PbI_2 was investigated. For this purpose two samples of PbI_2 powder were heated to 200^oC and 300^oC respectively. Until further use, the samples were kept in a dessicator above P_2O_5. According to the above described procedure 40 experiments with thermally treated PbI_2 particles were performed to assess its ice-nucleating ability. The results of experiments with PbI_2 particles heated to 200^oC, 300^oC and not thermally treated are graphically represented in figs. 1a, 1b and 1c. It is apparent that the heating of PbI_2 decreased the temperature limit necessary for ice formation on the surface of the PbI_2 particles. The mean temperature of ice formation is approximately -4.0^oC for thermally untreated samples and in the ranges from -9^oC to -10^oC and from -11^oC to -12^oC for PbI_2 samples heated to 200^oC and 300^oC, respectively. It was observed that, after heating the PbI_2 sample to 300^oC, the majority of the cases (about 80%) in which the ice was formed on the particle surface fall in the narrow temperature range from -11^oC to -12^oC. We can presume that heating to this temperature results in changes in the particle structure which leads to the attainment of higher uniformity of the particle surface and consequently to poorer nucleating ability. A detailed investigation of the mechanism of this process is outside the scope of this work. We can assume that this process is related to adsorption of water molecules on crystal faces; under the effect of crystal lattice these molecules tend to become organized in an ice-like structure / 1 /. Edwards and Evans / 2 / came to the conclusion that water molecules adsorbed on the crystal surface of some ice-nucleating agents are essential for their nucleating properties. Above authors assumed that water molecules adsorbed on the crystal surface are in a disorganized state at temperatures above a certain critical temperature and in an organized state below that temperature. This assumption is in agreement with the observations of other authors / 3 /,/ 4 / which confirmed the relation between the activity of ice-nuleating agents and the humidity of the ambient air.

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TABLE 1.

Occurrence of freezing at various experimental conditions.

Exp. No.	T_o	T_s	Result [a)]
1	-2.8	-0.7	0
2	-7.0	-0.7	+
3	-7.7	-0.9	+
4	-3.5	-0.8	0
5	-6.6	-1.0	+
6	-5.4	-0.9	+
7	-4.8	-1.0	+
8	-5.2	-0.6	+
9	-4.3	-0.6	+
10	-2.1	-0.9	0
11	-4.5	-0.8	0
12	-4.6	-0.9	+
13	-5.4	-0.8	0
14	-6.3	-0.4	+
15	-6.6	-0.5	+
16	-6.8	-1.0	+
17	-5.2	-0.8	0
18	-6.8	-0.3	+
19	-7.7	-0.2	+
20	-3.2	-1.0	0
mean value	-3.80	-0.85	0
	-5.80	-0.65	+

a) 0 did not freeze

\+ froze

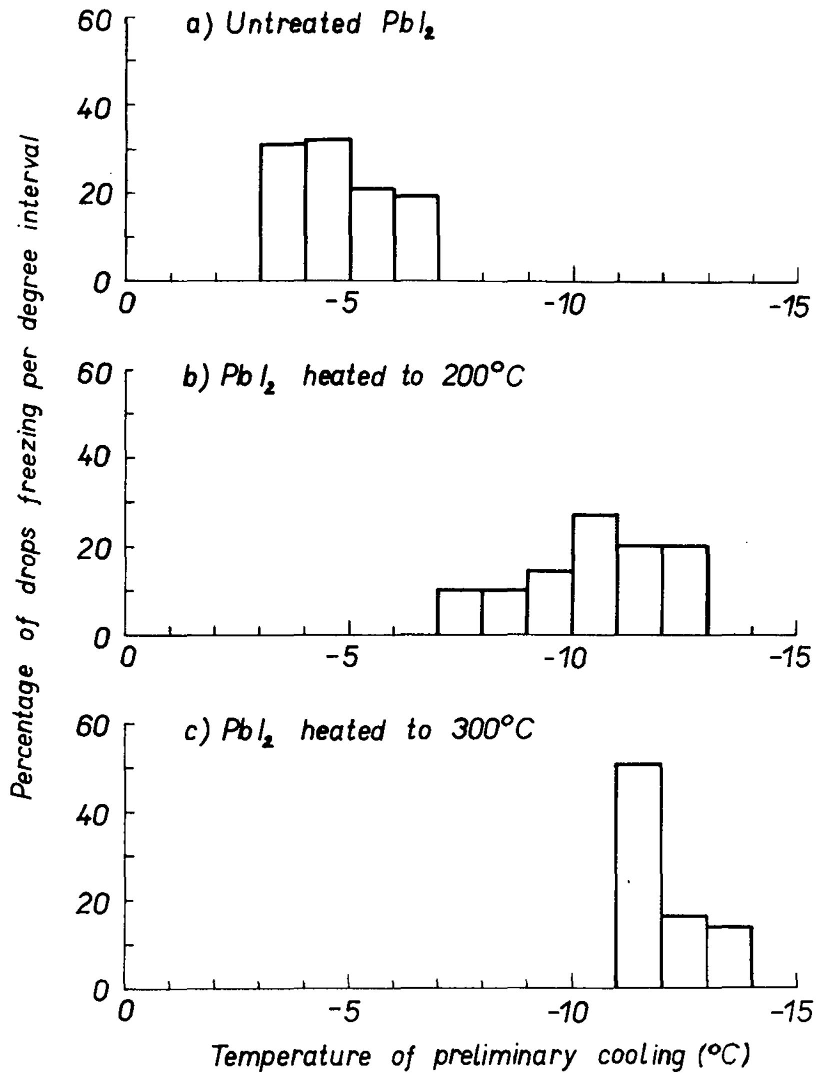
TABLE 2.

Frequency of freezing of droplets in various temperature ranges.

T_o (^oC)	cumulative frequency of freezing events (%) [a]	increase in freezing frequency in given range
Above -3.1^o	0	-
from -3.1^o to -4.0^o	30	30
from -4.1^o to -5.0^o	61	31
from -5.1^o to -6.0^o	81	20
from -6.1^o to -7.0^o	100	19

[a]) to the lower temperature limit of the given range

FIGURE 1



Histogram of preliminary cooling temperature vs percentage frequency of drops freezing per degree Celsius interval.