Urea as an Ice Nucleant for Supercooled Clouds

ROBERT G. KNOLLENBERG
The University of Chicago, Ill.
USA

Abstract
Urea was observed to have extraordinary ice nucleating properties in laboratory and natural clouds. Ice nucleation was induced in laboratory clouds at temperatures as warm as +6C. The nucleation mechanism involves the high endothermic heat of solution and high solubility of urea. Three field releases of urea in supercooled stratus resulted in marked visual transformation of the cloud and substantial snow showers. It is concluded that urea is an effective seeding reagent for supercooled clouds. In these experiments urea appeared to be equally effective as dry ice in causing shower formation.

Urea as an Ice Nucleant for Supercooled Clouds[1]

ROBERT G. KNOLLENBERG[2]

The University of Chicago, Ill.

ABSTRACT

Urea was observed to have extraordinary ice nucleating properties in laboratory and natural clouds. Ice nucleation was induced in laboratory clouds at temperatures as warm as +6C. The nucleation mechanism involves the high endothermic heat of solution and high solubility of urea. Three field releases of urea in supercooled stratus resulted in marked visual transformation of the cloud and substantial snow showers. It is concluded that urea is an effective seeding reagent for supercooled clouds. In these experiments urea appeared to be equally effective as dry ice in causing shower formation.

1. Introduction

Within the last few years the number of chemical compounds found to induce heterogeneous nucleation of ice in supercooled clouds has been supplemented by a large variety of organic compounds. Among the contributions to the literature are those of Fukuta (1965), Fukuta and Mason (1963), and Langer *et al.* (1963). Organic compounds, such as cholesterol and phloroglucinol were found to be active in laboratory clouds at relatively warm temperatures ($-2C$ to $-3C$). However, field testing of some of these compounds, e.g., phloroglucinol, has not proven them to be as effective as dry ice or silver iodide for seeding supercooled clouds (Braham, 1963).

Recent studies in the Cloud Physics Laboratory of the University of Chicago have shown that urea is another organic compound that has very interesting and possibly important properties as an ice nucleant. Urea, or carbamide (NH_2CONH_2) was one of the first organic compounds to be synthesized from inorganic compounds. It is largely used as a fertilizer, but it also has important industrial applications. It exists as colorless tetragonal crystals at room temperature with a density of 1.335 gm ml^{-1}. The melting point of urea is 132.7C, and it decomposes to ammonia and carbon dioxide with further heating. Urea is also hygroscopic and very soluble in water [78 gm (100 ml)$^{-1}$ at 5C]. The process of dissolving one gram of urea in water is accompanied by the absorption of 60.5 calories of heat. Our studies show clearly that the ice nucleating properties of urea depend upon its endothermic heat of solution and high solubility.

The ice nucleating properties of urea were first ob-

served in our laboratory when sizable quantities of the compound were found to nucleate drops at temperatures above $-5C$. The drops (1 mm radius) were suspended from a thermocouple in a laboratory cold box. The amounts of urea required to nucleate these large drops would seem to limit its effectiveness as a seeding reagent, but further investigations were prompted when the literature revealed a threshold temperature for ice nucleation of $-18C$ for urea (Langer *et al.*, 1963).

These investigations first took the form of dispersing finely powdered urea into a Bigg-Warner ice nuclei counter operated in a conventional manner. It was found that urea was an effective ice nucleant at $-10C$ and even partially active above $-3C$. After a slight modification in the operating procedure to produce a more dense water cloud in the chamber, crystal counts were observed in the supercooled sugar solution at cloud temperatures of $+6C$. This unusual phenomenon prompted further investigations which are detailed in the next section of this report.

It was also decided that field investigations were necessary to determine the effectiveness of urea as a seeding reagent under natural cloud conditions. Plans were already underway to test hydrophobed silicates prepared by A. C. Zettlemoyer, Lehigh University. The field testing of urea was immediately added to that objective. These tests took place during the final two weeks of February 1965.

2. Laboratory investigations involving urea

The procedures used to study the ice nucleating properties of urea were:

1. The Bigg-Warner chamber, provided with a thermal insulating liner covering the vertical walls but not the bottom, was cooled to $-5C$ to supercool the sugar solution (33 per cent, 1.14 sp. gr.).

[2] Graduate student from University of Wisconsin, under CIC Traveling Scholar Program for period October 1964–January 1965.

2. A cloud of desired temperature was produced by breathing heavily into the chamber (thermo-couples were used to measure the air temperature inside the chamber).

3. A small amount of milled urea was drawn into the chamber through the purging hose.

4. The cloud temperature at which the first ice crystals were observed in the sugar solution was taken to be the threshold temperature for ice nucleation.

It was found that urea could induce ice nucleation as detected by a supercooled sugar solution, at cloud temperatures ranging from +6C to below −15C. Obviously any ice crystals formed at temperatures above 0C would begin to melt very rapidly, but it was found that some of them survived long enough to fall into the supercooled sugar solution at the bottom of the chamber.

In many experiments the urea would exhaust the water cloud prior to the time that all ice crystals grew sufficiently to fall into the sugar tray. In these cases additional breathing into the chamber would produce additional ice crystals in the supercooled sugar solution.

In spite of the fact that ice crystals were detected in the supercooled sugar solution at cloud temperatures of +6C, the warmest temperature at which they were visually detected, within the cloud, in the Bigg-Warner chamber was −8C. Our interpretation of these observations is that compounds which are very soluble, hygroscopic, and have high endothermic heats of solution may not initially form ice crystals that will allow visual detection easily, within a cloud, as by scintillation in a beam of light. Initially, it is more likely that they act as condensation nuclei and form droplets. Before the entire urea crystal dissolves it nucleates the droplet forming a miniature sleet pellet which obviously does not have the required crystalline faces to produce reflection.

The possibility that dry particles or cold solution droplets were nucleating the supercooled sugar solution was checked and ruled out. However, solution droplets containing ice crystals were found to nucleate the supercooled sugar solution.

To explain the ice-nucleating properties of urea one must consider the calorimetry problem involving its heat of solution which is −60.5 cal gm⁻¹. As urea is dissolved in water it cools the solution until it reaches a temperature at which it is saturated. Provided the initial temperatures of the urea and water are low enough, the solution will either supercool below its eutectic point (−11.5C) or ice will crystallize out at the eutectic point. By adding excess urea to water in a dewar flask it was found that ice crystals began to form at a solution temperature of −11.5C, providing the initial temperatures of the urea and water were below certain critical values. These critical values of the initial temperatures of the urea and water can be
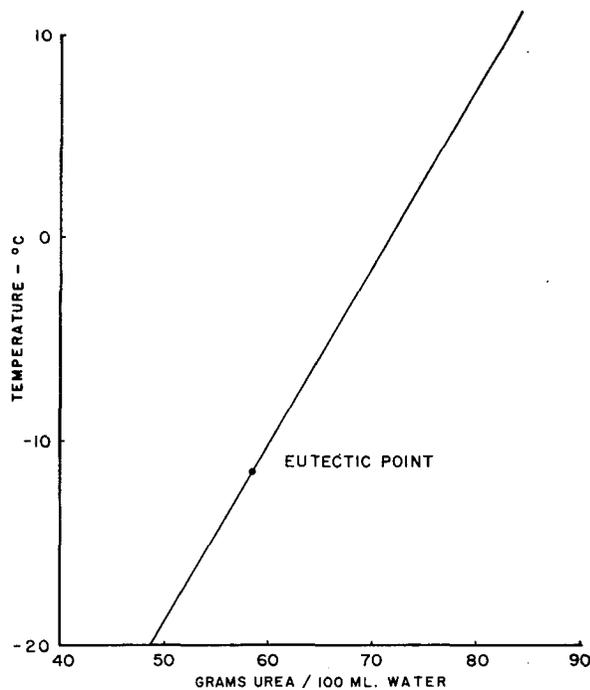

Fig. 1. Solubility of urea.

calculated making use of the following symbols and technical data about urea and water:

$T_i =$ initial temperature of urea and water,
$T_0 =$ eutectic point, −11.5C,
$C_u =$ specific heat of urea, 0.32 cal gm⁻¹ (°C)⁻¹,
$C =$ specific heat of water, 1.00 cal gm⁻¹ (°C)⁻¹,
$H_s =$ heat of solution of urea, −60.5 cal gm⁻¹,

The solubility of urea is 58.5 gm (100 ml)⁻¹ H₂O at −11.5C. See Fig. 1. Using the assumption of an ideal solution we can set up the following equality describing the heat exchange when urea dissolves:

$$100(T_0 - T_i)C + 58.5(T_0 - T_i)C_u = 58.5 H_s. \qquad (1)$$

On solving for T_i, we find $T_i = 18.3$C. This means that if care is taken to insulate the calorimeter, ice crystals can be produced from dissolving urea in water with initial temperatures nearly as warm as +18.3C.

In the experiments involving the Bigg-Warner chamber, particles of milled urea were dispersed into a cloud of water droplets. Some of the urea particles collided with water droplets whereupon nucleation occurred by the same process as that observed with the drops suspended from the thermocouple in the initial tests. The urea particles that did not collide with droplets probably acted as condensation nuclei forming growing droplets which also appeared to be nucleated after a short period of growth.

Whether nucleation occurs upon collision of droplets with urea particles or after growth by condensation upon the urea particle, the endothermic heat of solution of urea must be sufficient to cool a portion of the
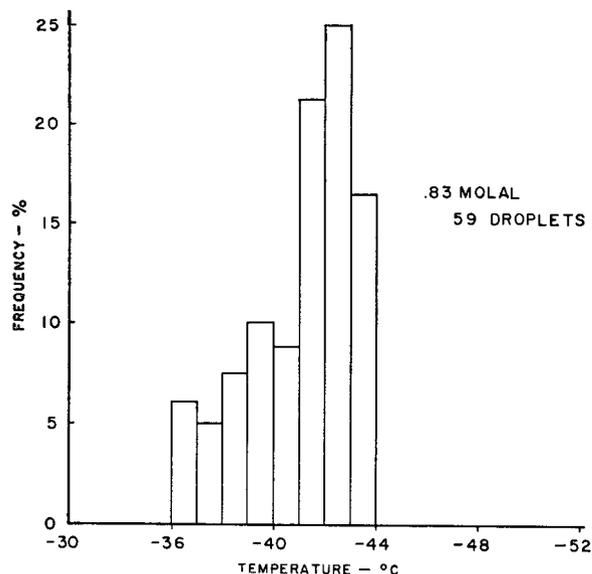
FIG. 2. Frequency diagram of freezing temperatures of droplets of an 0.83 molal urea solution.

TABLE 1. Comparison of the epitaxy of urea.

Crystal class		Lattice constants, Ångstroms		Basal misfit per cent	Prism misfit per cent
		a	c		
Ice	hexagonal	4.52	7.36	—	—
AgI	hexagonal	4.58	7.49	1.4	1.6
Urea	tetragonal	5.67	4.73	—	13.9

droplet below its freezing temperature. We determined the freezing temperatures of urea solution droplets using a method developed by Hoffer (1961). Solution droplets 100–120 microns in diameter, suspended in silicone oil, were frozen and the temperature monitored with a thermocouple. Droplets of 0.83 and 6.7 molal urea solutions were observed to have median freezing temperatures of $-42C$ and $48.7C$, respectively, as shown in Figs. 2 and 3. Hoffer's value for the median freezing temperature of pure water droplets of similar size was $-36C$.

It is apparent from these results that the amount of cooling produced by the endothermic heat of solution of urea is insufficient to lower the temperature of
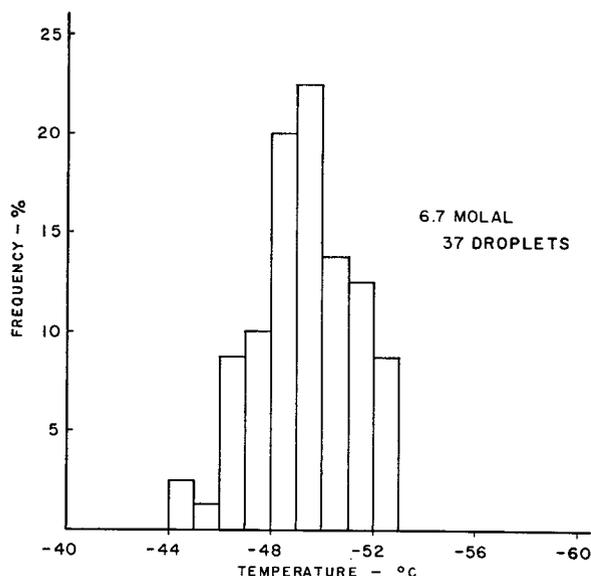

FIG. 3. Frequency diagram of freezing temperatures of droplets of a 6.7 molal urea solution.

droplets in the Bigg-Warner chamber to the observed freezing temperatures of the most dilute solution droplets. Therefore the observed crystals could not have been nucleated by freezing of solution drops.

To explain the observed ice nucleating properties of urea it appears necessary to assume that nucleation takes place by epitaxy on the surface of the urea in the fluid boundary layer immediately adjacent to the dissolving urea particle. It is quite reasonable to assume that this boundary layer is cooled nearly as much as found calorimetrically for the bulk solution. The dissolving urea particle then most likely nucleates this locally cooled region. For this explanation to hold it follows that the epitaxial threshold temperature of urea must be above the temperature of the cooled solution in the boundary layer.

Due to the large endothermic cooling resulting from a dissolving urea particle, the epitaxial threshold temperature of urea need not be very high for nucleation to occur at relatively warm cloud temperatures. It follows that the epitaxy of urea might vary considerably from that of ice. In Table 1 a comparison is made of the crystal lattices of ice, urea, and silver iodide. No attempt was made to calculate the basal misfit by matching the hexagonal face of ice to a face of the tetragonal urea crystal. The best prism misfit amounts to about 14 per cent which is much larger than that of silver iodide and other good ice nucleants.

The exact epitaxial threshold temperature of urea is not known and would be difficult to determine experimentally. From observations of supercooling of eutectic solutions, when excess urea was added to water, the epitaxial threshold temperature of urea appeared to be well below its eutectic point. If one assumes that $+6C$ is the maximum temperature at which urea will induce nucleation, as found in our laboratory, the epitaxial threshold temperature of urea can be estimated by simply calculating the lowest temperature to which a dissolving urea particle is cooled. To perform this calculation the solubility of urea must be expressed as a function of temperature. For temperatures below

TABLE 2. Milled urea size distribution.

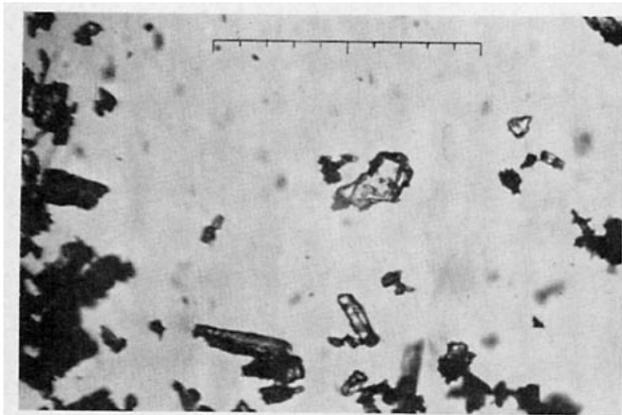| Size class (microns)	Number of particles per gram
<25	5.4×10^7
25–49	2.0×10^7
50–74	2.4×10^6
75–99	0.1×10^6
>100	0

FIG. 4. Microphotograph of milled urea. Smallest scale division equals 10 microns.

FIG. 5. Sun dog in cloud seeded with milled urea. See Table 3.

0C the solubility is given approximately by the linear expression $(72+1.17T)$ grams of urea per 100 ml H_2O. Using the technical data preceding Eq. (1), we can set up the following equality:

$$100(T_e-T_i)C+(72+1.17T_e)(T_e-T_i)C_u$$
$$= (72+1.17T_e)H_s, \quad (2)$$

where T_i now has the value of $+6C$ and T_e is the epitaxial threshold temperature. An epitaxial threshold temperature of $-20C$ results.

In summary, the ice nucleation problem of urea might be thought of as analogous to that which occurs when dispersing nucleants in a solvent that produces an evaporative cooling upon spraying (Fukuta, 1965). The cooling effect of the endothermic heat of solution of urea is similar to the evaporative cooling effect of the solvent. In both cases the solid particle is cooled to a temperature at which it becomes an active ice nuclei.

Once nucleation has occurred, there remains the possibility that the ice crystals will melt after reaching thermal equilibrium with the environment.

3. Preparation of urea for field testing

The urea used in the laboratory and two of the three field experiments described herein, was donated by the

W. R. Grace Chemical Co., Chicago, Illinois. A purer industrial grade of crystalline urea was used in all experiments, instead of the more common fertilizer urea. The lower moisture content (0.05 per cent) of the industrial grade was thought to be necessary to reduce clumping after the urea was milled. The crystalline urea was received in 100 pound paper bags that were not air-tight; therefore the moisture content is questionable. As received the urea consisted of crystals ranging from 2 mm diameter to 100 microns diameter, with a mean diameter of 550 microns.

Since our laboratory experiments indicated that submicron particles were active in the Bigg-Warner chamber, 70 pounds of the original crystalline urea were ball-milled resulting in particles ranging from 100 microns diameter to less than 5 microns in diameter with a mean diameter of 25 to 30 microns. The milling produced 10^7 to 10^8 particles per gram. The size distribution of the milled urea was obtained with a sieve separator and is given in Table 2. A microphotograph of a representative sample is shown in Fig. 4. The milled urea was packaged in polyethylene bags in 10 pound samples for later release.

A sample of the milled urea was tested in a wind tunnel to determine to what extent clumping might occur when the milled urea was manually dumped into the airstream from aircraft. These tests indicated that

TABLE 3. Preliminary results of three field experiments.

Date	Release	Location	Cloud	Seeding rate	Seeding temperature	Results
15 Feb 65	#1 (milled urea)	15 miles N Ladysmith, Wisconsin	Stratus Top 6.7K Base 2.5K LWC .5 gm m^{-3}	9.3 lb. per mile	$-16.1C$	Hole developed with appearance of sundogs (Fig. 5). Heavy snow shower to ground.
17 Feb 65	#2 (milled urea)	25 miles ESE Duluth, Minnesota	Stratus Top 6.0K Base 3.3K LWC .6 gm m^{-3}	4.8 lb. per mile	$-13.8C$	Very dense snow shower and broken hole in cloud (Fig. 6).
26 Feb 65	#3 (unmilled urea)	33 miles SE Eau Claire, Wisconsin	Altostratus Top 10.8K Base 9.8K LWC .2 gm m^{-3}	12.2 lb. per mile	$-13.1C$	Well defined snow shower that was strongly sheard by wind below cloud base (Fig. 7).

FIG. 6. Intense snow shower with a developing hole resulting from seeding with milled urea. See Table 3.

FIG. 7. Strongly sheared snow shower resulting from seeding with unmilled urea. See Table 3.

clumping would not be a serious problem. This was verified in two of the three field experiments which used the milled material.

In the third field experiment a chemical reagent grade of urea was used, which was purchased from the Mallinckrodt Chemical Co. This urea had a mean particle size of about 150 microns in diameter.

4. Preliminary results of urea seeding

A series of three tests of urea as a seeding reagent for supercooled clouds was carried out on 15, 17 and 26 February 1965 in the off-airways areas of central and northern Wisconsin. The Project Whitetop instrumented twin Beechcraft airplane was used for releasing the urea and for monitoring the results.

In the field experiments the urea was manually released by allowing it to flow out of a four inch plastic tube that was fitted into a hole in the fuselage of the airplane. Twenty pounds of urea were dropped in each of the field releases. Although it was very difficult to maintain an even flow rate, the average rate of seeding was between 5 and 10 pounds per mile. In all releases the urea was released in the upper 200 feet of cloud.

From previous experience it was thought advisable to use dry ice drops as an aid to navigation when testing unproven reagents (Braham 1963). A dry ice drop was made in the first field experiment but was not used in subsequent ones because of marked visual effects accompanying the transformation of the supercooled clouds following urea seeding.

The results of the three field experiments are tabulated in Table 3. The specific information for each release includes the seeding rate, temperature of seeding, liquid-water content, cloud thickness, general cloud features and description, and the results of the seeding. The photographs of Figs. 5–7 are also included to support the results.

5. Conclusions

Urea appeared to be as effective as dry ice for seeding supercooled clouds at the temperatures at which the

releases were made. The milled urea was much more effective than the unmilled, as expected. The nucleation appeared to be almost instantaneous, especially in the third release. From the intensity of the observed snow showers the percentage of urea crystals resulting in ice crystals was probably high.

In all three of the field experiments the clouds were relatively cold. In our experiments the urea was milled to a particle size resulting in approximately 10^8 particles per gram. By comparison, the activity spectrum of the best silver iodide burner shows that the number of active silver iodide particles decreases to a value of less than 10^8 particles per gram at a temperature between $-4C$ and $-5C$ (Fletcher, 1959). It would appear that, in terms of the number of active particles, any advantage of using urea as a seeding reagent would be at temperatures above $-5C$. The immediate objective of the continuing experimentation is to seed clouds just below 0C.

In conclusion the results are quite striking. Urea is now established as a very promising seeding reagent. Its efficacy can undoubtedly be improved simply by milling it to a smaller particle size.

REFERENCES

Braham, R. R., Jr., 1963: Phloroglucinol seeding of undercooled clouds. *J. Atmos. Sci.*, **20**, 563–568.
Fletcher, N. H., 1959: The optimum performance of silver iodide generators. *J. Meteor.*, **16**, 385–387.
Fukuta, N., 1965: Activated ice nucleation by sprayed organic solutions. *J. Atmos. Sci.*, **22**, 207–211.
——, and B. J. Mason, 1963: Epitaxial growth of ice on organic crystals. *J. Phys. Chem. Solids*, **24**, 715–718.
Hoffer, T. E., 1961: A laboratory investigation of droplet freezing. *J. Meteor.*, **18**, 766–778.
Langer, G., J. Rosinski and S. Bernsen, 1963: Organic crystals as icing nuclei. *J. Atmos. Sci.*, **20**, 557–562.