

Organic Crystals as Icing Nuclei

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ABSTRACT

Laboratory work showed that organic compounds have considerable promise as cloud-seeding agents. The following substances gave complete nucleation: phloroglucinol at -2°C , trichlorobenzene at -12°C , D(+)-Raffinose at -14°C , trimesic acid at -15°C , and melamine at -15°C . Thirty-two organic compounds were investigated. The tests were conducted in a deepfreeze cloud chamber and a Bigg-Warner chamber. Field tests by the University of Chicago (Braham, 1963) confirmed the activity of phloroglucinol.

Theoretical analysis indicates that activity of organic icing nuclei is determined by configuration of electric link-dipole moments in the molecule.

1. Introduction and experimental procedure

On the basis of preliminary tests (Langer, 1959), this systematic study of organic compounds (Langer and Rosinski, 1962) was initiated in the fall of 1961. At that time the work of Komabayashi and Ikebe (1961) was the only other reference found. Therefore, the work was directed at surveying a wide variety of organic compounds, and at the same time developing a theory that would help in selecting future compounds. Promising materials were to be adapted for field use.

A Bigg-Warner chamber as modified by Kline (1961) and a horizontal deepfreeze cloud chamber were selected for testing nuclei. The Bigg-Warner unit served as the reference instrument because it is in wide use. The chamber in Fig. 1 was operated continuously and made possible a realistic evaluation.

The Bigg-Warner chamber consists of a refrigerated space. The chamber is filled with an aerosol of the test substance, pressurized with clean air, and suddenly expanded. The adiabatic cooling produces a supercooled cloud. When active nuclei are present, they form ice crystals. The crystals settle into the supersaturated sugar solution and nucleate it to form large crystals. A few chemicals besides ice also initiate this process; therefore, each material is allowed to settle on the tray without expansion to test for interference.

The sugar (sucrose) solution retards the speed of crystallization of water to a remarkable degree, and the freezing of the nucleated spot of solution can be distinguished. The number of ice crystals produced is estimated simply by counting the easily visible ice crystals growing on the surface of the sugar solution. The sugar solution should be kept at -12°C . Adjustment of the expansion ratio controls the cloud temperature from -15 to -30°C . At higher temperatures cloud formation is erratic. The wall temperature should be

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above -10°C , or the sugar solution does not function properly.

The layout of the deepfreeze chamber is shown in Fig. 1. The fan, operated at a low speed, produces a relatively uniform temperature in the chamber. Supercooled droplets are formed by injecting steam into the chamber. The nucleation process is observed with a light beam shining into the chamber. To prevent nucleation by rime ice formed on the walls, the chamber is periodically coated with glycerine. A fog of heavy consistency is first formed; then the nuclei are added.

The organic compounds of interest were made into aerosols in a number of ways. A Wright dust feeder was used for dry dispersal. It uses an impinging air jet to disperse a compacted sample of powder. Water-soluble materials were atomized to form an aerosol. Upon evaporation of the water, the aerosol consisted of dry particles or, when the material was hygroscopic, of semiliquid droplets. The atomizer was a 0.5-cm stainless-steel tube, closed at one end, with a narrow slit (0.1 mm wide) cut into the tube near the closed end. An air pressure of 20 psi was applied to the jet. This pressure produced sonic flow in the slit, and fine atomization resulted. About 90 per cent of the droplets were smaller than $1\ \mu$ in diameter.

Aerosols were also produced by heating. Usually the air was preheated in a tube furnace and then passed through a bed of the organic powder. For some tests nitrogen was used as the carrier gas. Some of the compounds were dispersed directly by applying heat to a flask and passing air through it. The nuclei generators were adjusted to give a light bluish or white smoke when the nuclei-bearing gas stream was examined with a light beam.

The aerosols were sampled with a moving-slide impinger, a thermal precipitator, or a cascade impactor. The deposits were examined with a light microscope or an Hitachi HS-6 electron microscope.

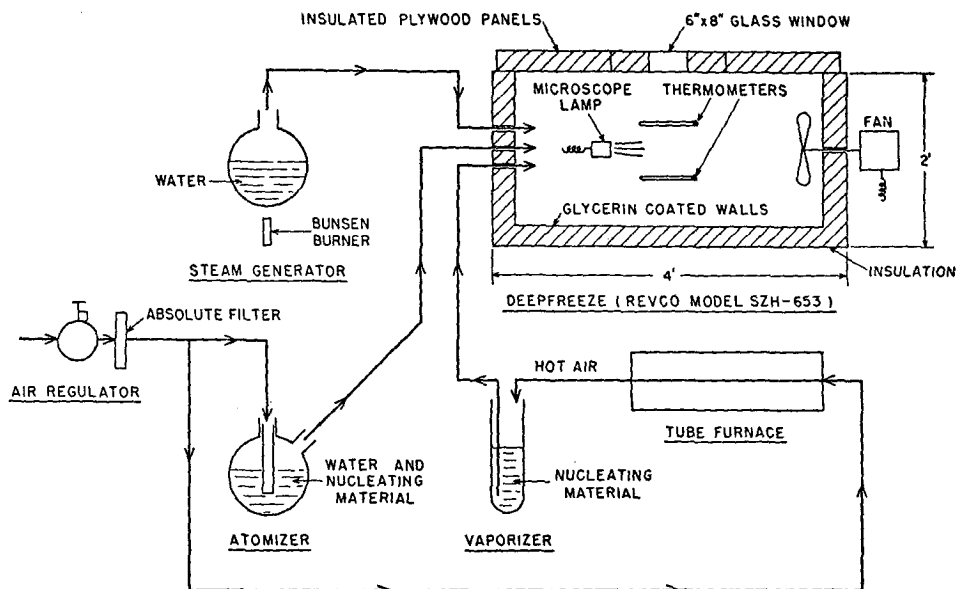


FIG. 1. Deepfreeze ice-nucleating chamber.

2. Survey studies of various organic materials

Table 1 summarizes the results from all the compounds tested in the two chambers. When complete nucleation occurred, the deepfreeze chamber was cleared of fog in about 1 min. When partial nucleation occurred, a considerable number of icing crystals appeared, i.e., the fog was not completely cleared but became noticeably more transparent. When slight nucleation occurred, a few large ice crystals were formed and the fog did not clear. The Bigg-Warner counts represent the total number of ice crystals formed in the chamber and served as an indication of potential activity. If the number and size of the aerosol particles added are known, the over-all efficiency of the test substance can be determined. Dry ice and silver iodide, the reference substances, produced visible ice crystals in 2 sec at -4°C , and the fog was cleared after 15 sec in the freezer.

As a first step, previously investigated organic icing nuclei were tested. These compounds included furoic acid, melamine, urea, and salicylic acid, all of which were previously tested (Langer, 1959). The first three showed incomplete activity. Melamine achieved complete nucleation at the low temperature of -16°C , and was slightly active at -8°C . The reaction was slow, i.e., more than $\frac{1}{2}$ min elapsed before nucleation became evident at -16°C . Care had to be taken that the larger organic crystals from the aerosols were not mistaken for ice crystals.

A number of the aromatic compounds studied by Komabayashi and Ikebe (1961) were also studied. These included sucrose, naphthalene, pyrogallol, anthraquinone, phthalic acid, and terephthalic acid. None of these showed significant activity, although the last four

compounds were active at -16°C . Only pyrogallol cleared the box when taken to -25°C . The dispersal methods may have an effect on the results. Komabayashi and Ikebe dispersed the dry powder as relatively large particles, 3 to $10\ \mu$ in diameter. We used heat for these chemicals to produce mostly submicron particles.

Data in Table 1 can be compared with results by Head (1962). His interest was in steroids as ice nucleators, but he also considered other compounds in less detail. He found naphthalene to be inactive above -20°C , and our results agree with this. However, α - and β -naphthol were considered by him to be relatively active although we found no useful activity. Head found no active halocarbon compounds, but trichlorobenzene was found to nucleate in our work.

Phloroglucinol was tested on the basis of the work of Bashkurova (1957), whose paper was discovered during the program. Our initial results agreed with hers; i.e., the substance nucleated completely at -8°C . It was therefore selected for more detailed studies after the screening of additional compounds was completed. The other compounds listed in Table 1 were selected on the basis of theoretical work described in Section 4. None of these were active above -10°C . The activity of D(+)-Raffinose and of trichlorobenzene was of interest because it suggests a new series of compounds.

3. Detailed studies of phloroglucinol

Phloroglucinol, the most promising substance, was tested further. Improved nuclei-generation procedures gave especially good results. Phloroglucinol acted after 10 sec at -2°C to give easily noticeable crystals, and the chamber was cleared of fog after 50 sec when either a

TABLE 1. Results of nucleation tests with organic substances.

Name	Formula	Material	mp, C	bp, C	Solubility, parts per 100 parts H ₂ O	Complete	Deepfreeze Temp., C	Slight	Nucleation Maximum nuclelet count/10 liters	Bigg-Warner	Temp., C
Room air											
Acetophenone	CH ₃ COC ₆ H ₅		19.6	202	insol.				0		-15
1-Aminoanthraquinone	C ₁₄ H ₉ (CO) ₂ C ₆ H ₄ NH ₂		286	subl.	insol.				21		-19H*
Anthraquinone-9,10	(C ₆ H ₄) ₂ (CO) ₂		286	379-81					0		H*
Azobenzene	C ₆ H ₅ N ₂ C ₆ H ₅		68	297					200		-18H*
Benzl.	(C ₆ H ₅ CO) ₂		95	346-8					80		-18H*
Benzoin	C ₆ H ₅ CHOHCOC ₆ H ₅		133-7	343-4 at 768 mm. v. sl. sol., hot					1000, 450		-18, -12H*
Cyanuric acid	(HNCO) ₃ ·2H ₂ O		>360	decomp.	0.27 at 17°				0		H*
Dextrose	CH ₂ OHCHO(CHOH) ₂ CHOH		146		sol.				0		S*
1,1-Diphenyl-2-thiourea	(C ₆ H ₅) ₂ NCSNH ₂		219, decomp.						0		S*
Furoic acid	C ₆ H ₅ COCOOH		133-4	subl. 100; 230-2, 3.6 at 15°					112		-20H*
D-(+)-Galactose	C ₆ H ₁₂ O ₆ CHO			266.6 at 752 mm. v. sl. sol., cold					0		S*
8-Hydroxyquinoline	HOC ₆ H ₄ N		75-6						0		S*
Inulin	(C ₆ H ₁₀ O ₅) _n ·H ₂ O		160, decomp.		0.01 at 0°				0		S*
Lactose	C ₁₂ H ₂₂ O ₁₁ ·H ₂ O		203.5, decomp.						0		S*
d-Levulose	H = C(NH ₂)N = C(NH ₂)N = C(NH ₂)N = C(NH ₂)N		<250	subl.					2000, 7		-25, -18H*
Melamine											-15SH*
Naphthalene	C ₁₀ H ₈		80.2	218.0	0.003 at 25°				0		H*
o-Naphthol	C ₁₀ H ₇ OH		96, subl.	278-80	sl. sol., hot				0		S*
β-Naphthol	C ₁₀ H ₇ OH		122-3	285-6	0.10 c.				0		S*
5-Nitrobenzimidazole	HNOCH = NC ₆ H ₄ ·NO ₂		204		sl. sol.				0		S*
Phloroglucinol	C ₆ H ₃ (HO) ₃ ·2H ₂ O		117	subl.	1.13 at 25°				5000, 3000, 500		-16, -12-10HS*
Phthalic acid	C ₆ H ₄ (COOH) ₂		191	subl.	0.54 at 14°				0		H*
Phthalic anhydride	C ₆ H ₄ (CO) ₂ O		130.8	284.5	v. sl. sol.				0		H*
Pyrogallic acid	C ₆ H ₃ (OH) ₃		133	309					0		H*
D-(+)-Raffinose	C ₁₈ H ₃₂ O ₁₆ ·5H ₂ O										-25H*
Salicylic acid	HO-C ₆ H ₄ -COOH		159	subl. 76							-23H*
Silver iodide	AgI		522, decomp.		3 X 10 ⁻⁷				0		S*
Sucrose	C ₁₂ H ₂₂ O ₁₁		170-186						0		H*
Terephthalic acid	C ₆ H ₄ (COOH) ₂		subl.						0		S*
1,3,5-Trichlorobenzene	C ₆ H ₃ Cl ₃		63.5	208.5 at 764 mm. sl. sol.					<5000, 1000		-17, -14H*
1,2,4-Trichlorobenzene	C ₆ H ₃ Cl ₃		17	213	insol.				20		-18H
Trimesic acid	C ₆ H ₂ Cl ₃ (COOH) ₃		375-80						50		-18H*
sym-Trioxane	OCH ₂ OCH ₂ OCH ₂		64	subl. 40					0		-18H*
Urea	NH ₂ CONH ₂		132.7	decomp.	100 at 17°				0		-18H*

* Method of dispersal: H, heating; S, slit-jet atomizer; W, Wright dust feeder.

dry dispersion or an atomized solution was used. When the phloroglucinol was atomized from a concentrated alcohol solution, only 20 sec was needed for clearing and the induction period (time elapsed before crystals were visible) was 4 sec at -2°C .

To nucleate effectively with drops of a water solution, the phloroglucinol must first precipitate. Precipitation was studied under the microscope by using a Thomas-McCrone cold stage. Dry cold nitrogen was passed over a microscope slide in a small enclosure. Small drops did not freeze until the crystals precipitated. When a crystal of phloroglucinol was dropped on a water drop, it froze instantaneously below 0°C . With a solution that precipitated before the freezing point was reached, freezing took place at 0°C . When a crystal of trimesic acid was added, no solidification occurred until -12°C . When a 0.013 g per ml phloroglucinol solution was cooled in bulk to $+11^{\circ}\text{C}$, crystals formed. A 0.0032 g per ml solution showed no crystals until it froze as a bulk at 0°C .

Examination of the phloroglucinol particles in the electron microscope gave inconclusive results. The substance was affected by the heat from the electron beam. When examined in room air under the light microscope, the particles looked like viscous droplets due to their absorption of moisture. To obtain crystal-shape data, electron microscope replicas should be made in a dry atmosphere. Detailed studies were made of phloroglucinol because it is the most promising substance. The factors considered were efficient means of dispersal, effect of solar ultraviolet, storage problems, toxicity, and anticipated consumption for seeding.

As far as can be ascertained, phloroglucinol is not especially toxic. The only necessary caution is to avoid direct ingestion. The commercial grade of the compound, which is brownish in color compared to the white c.p. grade, was effective for nucleation purposes. The commercial grade costs \$5.75 per pound in 100-lb fiber drum lots. It has 2 per cent ash and 25.5 per cent moisture. The technical grade costs \$8.25 per pound in 100-lb quantities. The c.p. grade costs \$12.95 per $\frac{1}{4}$ pound.

A sample of the commercial grade powder was exposed to ultraviolet light from a focused, unfiltered HB-200 Osram high-pressure mercury lamp for $1\frac{1}{2}$ hr. The exposure had no effect on its nucleating ability. When a solution was exposed for the same time it nucleated effectively, but after atomization for 15 min it lost its effectiveness. In both cases the chemical was atomized from a water solution. A solution of c.p. phloroglucinol discolored to a yellow-brown on standing for 3 days in fluorescent room light, but its nucleating ability was still good. Tentatively it seems that degradation due to ultraviolet is not a serious problem, considering the intense exposures used.

Tests were made to develop an efficient dispersal

method. To avoid degradation, air was heated in a $\frac{3}{8}$ -inch copper tube with a 150-watt heating tape. The hot air was then passed through a short bed of phloroglucinol in the tube instead of applying heat directly to the outside. Cold air was added immediately to condense the vapor into an aerosol. The output at 180°C bed temperature was run into the deepfreeze chamber for 2 min. Nucleation was very poor at -6°C . The particle concentration was over 10^7 per cc. Either the heat degraded the substance, or the particles were too small. The decomposition point is presumably above 200°C , the melting point range being 217 to 219°C .

Our conclusion was that the particle size was too small. This was verified by the fact that when phloroglucinol was heated in a flask by a Bunsen burner, good nucleation was achieved at -3°C when a white smoke issued from the flask. The color of the nuclei-bearing gas stream indicated particles in the 0.1- to $2\text{-}\mu$ range. With the first system the smoke was bluish and not very dense, indicating particles no larger than a few tenths of a micron. Further tests showed that the desired size for complete nucleation at -3°C was around $0.5\ \mu$.

With heat dispersal a fairly heavy smoke is desired for optimum nucleation in the 0- to -10°C range. The best system found so far can be scaled up for field use as follows. The powder as received is dropped onto a hot surface at a constant rate with a vibratory or screw feeder. The surface can be an inclined tube or a flat plate. It must be hot enough so the powder particles "dance" on it like drops of water on a hot griddle. That is, a gaseous film should form around the particles to avoid direct contact with the hot surface. This system needs further study before it is used on aircraft.

Larger quantities of prepared powder using the commercial grade of phloroglucinol were prepared as follows. The powder was ball milled for 24 hr as a water slurry. Then it was allowed to dry in air. The cake was broken up by hand and sifted through a 325 screen with an electric sieve shaker. To make the powder more free flowing, two to three times the volume of Cabosil was added to this and milled. The resulting powder was free flowing and was active at -2°C .

Tests were made to determine whether phloroglucinol produces a splintering effect (Krasikov, 1960) when dispersed in water droplets. That is, does a drop freeze and splinter into smaller pieces of ice? Known concentrations of nuclei were added to the Bigg-Warner chamber and the resulting number of ice crystals were counted. The ratio of the number of ice crystals to the number of nuclei varied from 0.02 to 0.1 ice crystals per nuclei in -10 to -20°C range. Therefore no multiplication of nuclei took place, but activity was high. These results showed no advantage in using a water solution unless large ice crystals were desired.

Consideration was also given to the use of organic solvents because they can accommodate much larger

concentrations. Tests were made with methyl alcohol of various strengths. It was dispersed with a DeVilbiss medicinal atomizer that uses a squeeze bulb. A regular atomizer could not be used because it released too much material and the alcohol or the denaturing agent poisoned the nuclei. A volume of 20 cc of aerosol from a 40 per cent solution completely nucleated and the deepfreeze chamber cleared at -3°C in 20 sec. The strongest water solution tested was 1 per cent, and about 2000 cc of aerosol from it was necessary for the same effect. Qualitatively this alcohol solution was by far the most effective release system tested. However, time did not permit a quantitative study of this procedure.

4. Proposed theory of action

Fletcher (1960) pointed out that efficiently nucleating crystal faces should have on their surfaces an equal number of ions of both signs. In such a case the orientation of dipoles on the surface is random, and the free-energy barrier which must be overcome to build an ice crystal embryo is at its lowest level. The first monolayer of water molecules is deposited randomly which corresponds to the normal orientation of molecular dipoles in an ice crystal.

The resultant dipole moment of an organic molecule is a property associated with the chemical bonds between atoms, that is, with the constituent link moments. If a molecule has central symmetry, it is nonpolar, i.e., the constituent link moments balance and do not produce a resultant electric dipole moment. Spatial distribution of vectors, corresponding to the constituent link moments should be considered, rather than the structural resemblance or crystalline similarity, when dealing with organic ice nuclei.

The crystallographic structure of ice is usually reported as hexagonal. Pauling (1960) has stated that the ice structure is disordered: each oxygen atom is surrounded by four others arranged at the corners of an almost regular tetrahedron, and the actual symmetry is 3 m (Hermann-Mauguin notation).

Preliminary results of a systematic study show that the atomic structure and the symmetry of a nucleating crystal should be considered. Cyanuric acid, $\text{C}_3\text{N}_3(\text{OH})_3$, and its amide, $\text{C}_3\text{N}_6\text{H}_6$ melamine, have different symmetry. Melamine has the skeletal symmetry, $\bar{6}2\text{m}$; cyanuric acid, C. S. 2. Both tautomeric formulae of the compounds should not exhibit any resultant electric dipole vectors, but the presence of oxygen atoms in a slightly distorted molecule of cyanuric acid may result in the presence of an oriented dipole moment. Melamine shows nucleating properties; cyanuric acid does not exhibit them.

Some compounds with a benzene ring were examined. Trimesic acid, $\text{C}_6\text{H}_3-1, 3, 5, -(\text{COOH})_3$, did not exhibit strong nucleating properties. Detailed crystallo-

graphic structure was not found in the literature, but again the presence of the carboxyl group might cause formation of a resultant charge on the oxygen atom due to resonance of the molecule and may lead to the presence of a dipole moment. Of 1, 2, 4-trichlorobenzene and 1, 3, 5-trichlorobenzene, only the 1, 3, 5-trichlorobenzene should not have a resultant dipole moment. Because it belongs to the $\bar{6}2\text{m}$ class, it should possess nucleating properties. Indeed, 1, 3, 5-trichlorobenzene did exhibit ice-nucleating properties, but the 1, 2, 4-trichlorobenzene did not nucleate at all.

By replacing the chlorine with hydroxy groups in 1, 3, 5-trichlorobenzene, phloroglucinol was obtained. It had strong ice-nucleating properties. A resultant dipole moment did not exist, and the hydroxy groups were present which should simplify formation of an embryo on the $\bar{6}2\text{m}$ (skeletal) structure.

Benzoin (α -hydroxyketone), $\text{C}_6\text{H}_5\text{CHOHCOC}_6\text{H}_5$, which is hexagonal, has nucleating properties; but benzil ($\text{C}_6\text{H}_5\text{CO}$)₂ does not nucleate. The presence of a hydroxyl group in the organic molecule may be required to exhibit stronger ice-nucleating properties. Hydrogen-bonding properties, in general, have been suggested as important by Komabayashi and further emphasized by Head (1962). Power (1962) used amino acids (alanine, leucine, tryptophane and aspartic acid) and Head (1962) used α -phenazine, but there is no data to examine their nucleation properties from the standpoint of the theory of the electric link-dipole movements. In these amino acids, the NH_2 group is attached to the α -carbon of the COOH group and this would indicate again the importance of the hydrogen bond formation.

The experiments to date indicate that organic compounds which exhibit ice-nucleating properties should belong to a higher crystallographic class ($\bar{6}2\text{m}$) than ice (3m). Electric link-dipole moments should be arranged so that the molecule does not have a resultant dipole. In further studies distribution of positive and negative charges on the faces of organic crystals should be considered.

Phloroglucinol is relatively soluble in water compared with other ice-nucleating materials. Phloroglucinol also absorbs moisture from the air, and in laboratory tests it was active at the same temperature as silver iodide and was equally effective in clearing the test chamber. However, with silver iodide, ice crystals were seen in 1 or 2 sec, while with phloroglucinol up to 10 sec elapsed. Perhaps the material does not act by direct sublimation of water vapor ice on the nucleus, but instead a layer of liquid water may be formed before the chemical nucleates, or else direct collision with a water drop occurs.

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