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Silanes as Cloud Stabilizers

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ABSTRACT

Silanes (alkylchlorosilicon compounds) are effective in stabilizing cloud droplets against evaporation. Among 14 compounds tested, the alkyltrichlorosilanes proved most efficient in this role. The mode of action is apparently a reaction of the silane with water at the surface of a droplet to form a silicone polymer film that lowers the water vapor pressure over the surface. The reduction of vapor pressure was demonstrated by experiments, which showed that the dewpoint is lowered in a silane-treated cloud and over a silane-treated plane water surface. Substances that are effective as cloud stabilizers were also found to be effective in preventing the nucleation of ice crystals by AgI ice nuclei in a supercooled cloud.

SILANES AS CLOUD STABILIZERS

Charles C. Van Valin and Paul A. Allee

1. INTRODUCTION

One of the principal uses of silicon organic compounds is in waterproofing. These compounds can be used effectively on a wide variety of materials to make a surface so water-repellent that passage of water through the surface of even very porous materials is prevented (Smith and Cristol, 1966). A drop of organosilicon compound placed on the surface of water will spread to form a very thin film across the entire surface. Such a film applied to the water droplets comprising a cloud would retard the rate of transfer of water from small to large droplets, or retard evaporation of the cloud droplets when their environment is mixed with drier air, thus stabilizing the cloud.

The alkylchlorosilanes, containing only silicon, chlorine, carbon, and hydrogen, and tetrachlorosilane react vigorously with water. Thus, in the reaction between trimethylchlorosilane and water, the dimeric product is hexamethyldisiloxane plus hydrogen chloride:

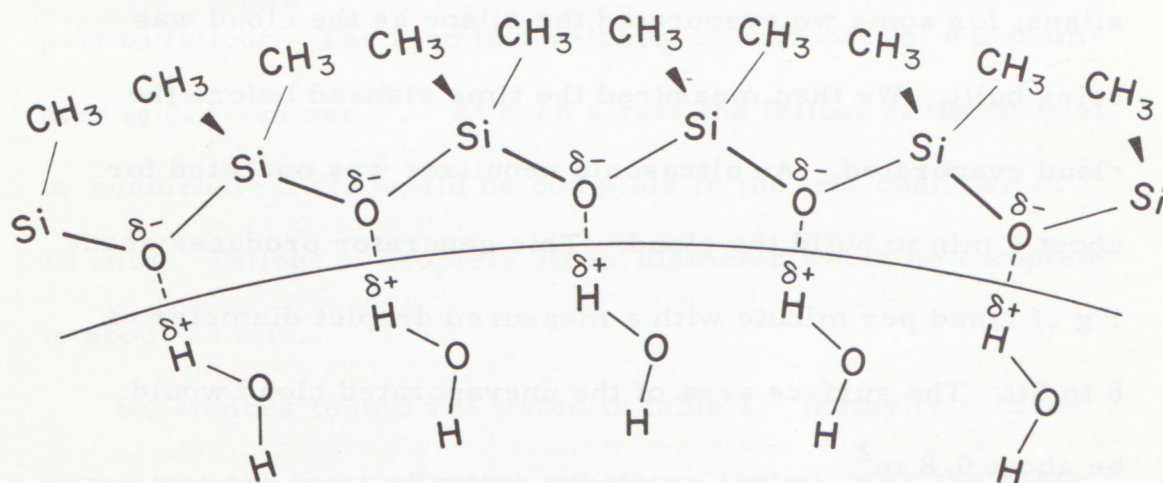


Figure 1. Representation of dimethylpolysiloxane coated on a water droplet. The methyl groups are arranged along one side of the linear molecule and impart the hydrophobic characteristics. The other side of the -Si-O- chain is exposed, accounting for the hydrophilic characteristics.

food freezer, where the temperature was maintained between -15 and -23°C, usually -16 to -18°C. For most of the tests we built a cloud in the freezer after having introduced the silane; for some we evaporated the silane as the cloud was being built. We then measured the time elapsed before the cloud evaporated. An ultrasonic nebulizer was operated for about 1 min to build the cloud. This generator produces about 1 g of cloud per minute with a measured droplet diameter of 6 to 8 μ . The surface area of the unevaporated cloud would be about 0.8 m².

A pure water cloud without any added substance endured from 3 1/2 to 6 1/2 min before evaporating completely to the walls--the period depending upon the temperature and the dryness of the freezer walls. With 20 μ l of the more effective substances, a moderate cloud was observed to remain 30 min, and a prominent Tyndall beam was visible even after 4 hr.

When there is an adequate moisture supply, a cloud can be generated within 4 or 5 min by evaporating 20 μ l or more of one of the most active chlorosilanes in the freezer. Such a cloud behaves the same way as clouds prepared with the nebulizer,

i. e., there is a gradual thinning that extends over a considerable time period.

The gradual thinning in a silane-treated cloud is due in part to fallout. The terminal velocity of a droplet of $6\ \mu$ diameter is $0.1\ \text{cm sec}^{-1}$. At such a rate the fallout of the droplet in nonturbulent air would be complete in the test chamber in 10 min. Fallout of droplets $3\ \mu$ in diameter would be complete in about 33 min.

Substances tested are listed in table 1. Methyltrichlorosilane was the most effective substance tested, with the other trichlorosilanes almost equal in performance. Dimethyldichlorosilane and tetrachlorosilane were slightly less effective. The homologs of these chemicals that contained only one chlorine atom were much less effective and those lacking chlorine were completely ineffective.

To determine if there would be any activity in the intermediate or final products of the reaction between water and trimethylchlorosilane, we tested chloromethyldimethylsilanol and hexamethyldisiloxane. The first compound is similar to the unstable intermediate, trimethylsilanol, but is more stable because of the chloromethyl group; the second is the final reaction

Table 1. Chemicals tested for cloud stabilizing action

Name	Formula	Boiling point (°C)	Amount tested (minimum)	Cloud life (min) (treated/untreated)	Relative Activity (scale of 0 to 5)
Dimethylsilane	$(\text{CH}_3)_2\text{SiH}_2$	-20	5 sec burst from pressurized can	4/4	0
Tetramethylsilane	$(\text{CH}_3)_4\text{Si}$	26.6	100 μl	4/4	0
Dimethylchlorosilane	$(\text{CH}_3)_2\text{SiHCl}$	36	10 μl	12/4	3
Trimethylchlorosilane	$(\text{CH}_3)_3\text{SiCl}$	59	1 μl	7/5	3
Dimethyldichlorosilane	$(\text{CH}_3)_2\text{SiCl}_2$	69.4	1 μl	13/5	4
Methyltrichlorosilane	CH_3SiCl_3	64.6	1 μl	25/5	5
Ethyltrichlorosilane	$\text{CH}_3\text{CH}_2\text{SiCl}_3$	100.5	1 μl	25/5	5
Allyltrichlorosilane	$\text{CH}_2=\text{CHCH}_2\text{SiCl}_3$	117.5	1 μl	25/5	5
n-Butyltrichlorosilane	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{SiCl}_3$	142	1 μl	25/5	5
Tetrachlorosilane	SiCl_4	57.6	2 μl	20/4	4
Chloromethyldimethylsilane	$\text{ClCH}_2(\text{CH}_3)_2\text{SiOH}$		100 μl	7/5	1
Diphenylsilanediol	$(\text{C}_6\text{H}_5)_2\text{Si}(\text{OH})_2$	mp 140 (decomp'n)	100 mg	45/5*	
Hexamethyldisiloxane	$(\text{CH}_3)_3\text{SiOSi}(\text{CH}_3)_3$	100	100 μl	7/5	1
Hexamethyldisilazane	$(\text{CH}_3)_3\text{SiNHHSi}(\text{CH}_3)_3$	126	100 μl	10/5	2
Hydrochloric Acid (36.5)	HCl		100 μl	6/4	1

*This result is considered unreliable because of the formation of decomposition products.

product. When applied at the maximum rate, each of these substances produced no more than a 50 percent increase in the cloud life.

Diphenylsilanediol was tested because it is similar in some respects to the very unstable intermediate from the reaction of dimethyldichlorosilane and water. The cloud treated with diphenylsilanediol lasted for up to 45 min. However, because considerable decomposition, with the production of smoke, occurred during vaporization, we cannot be sure that a stabilization of cloud droplets actually took place.

The reaction of the chlorosilanes with water liberates HCl. The presence of an electrolyte dissolved in the cloud droplets, such as the HCl generated by the reaction of the chlorosilanes with water, would lower the water vapor pressure over the droplets, stabilizing them to some extent (Twomey, 1959). To evaluate such an effect, we evaporated 100 μ l of concentrated hydrochloric acid from a warm watch glass in the freezer box at an air temperature of -20°C and built a cloud in the box. We found that this cloud lasted about 30 percent longer than an untreated cloud. Thus, the predicted stabilization does operate, but is of little significance when compared with the stabilization

effect from the reaction of chlorosilanes with the water droplet surface. The amount of HCl evaporated in this trial was approximately equal to the theoretical amount liberated by the reaction of 50 μl of methyltrichlorosilane with water.

The amount of methyltrichlorosilane applied was reduced from the usual 50 μl in an attempt to find the point at which further reduction in quantity would result in a marked reduction in the density of the cloud. The sample cloud containing about 1 g of liquid water was stabilized to the maximum extent in the 0.15 m^3 box with 20 μl or more of methyltrichlorosilane, but the density of the cloud was proportionately reduced when the amount of silane additive was reduced from 20 μl .

If one assumes the thickness of a monomolecular layer of silicone polymer to be on the order of $10 \overset{\text{O}}{\text{\AA}}$, only about 1 μl of silane could coat all the drops. The remaining silane would provide a thicker coating, thereby more effectively lowering the vapor pressure, or could react in the vapor phase. A vapor phase reaction could provide polymeric fragments capable of acting as condensation nuclei to generate droplets from the water vapor. Most of our tests were done at -16°C . At this temperature, the 0.15 m^3 space contains 0.19 g of water vapor, which is more

than 40 times the amount of water required for a complete reaction with 20 μ l of methyltrichlorosilane.

To test the relative effectiveness of the most active substances, we evaporated 1 μ l amounts into a cloud being built. One μ l of methyltrichlorosilane evaporated at -16°C stabilized the cloud to the extent that a faint Tyndall beam remained 25 min after generation. Under the same conditions, 1 μ l quantities of n-butyltrichlorosilane, allyltrichlorosilane, and ethyltrichlorosilane produced the same degree of stabilization; the cloud containing 1 μ l of dimethyldichlorosilane thinned to the same extent in less than 15 min, and with 1 μ l of trimethylchlorosilane similar depletion occurred in about 7 min. An untreated cloud lasted 5 min.

2.2 Effect on Vapor Pressure

The lowering of the vapor pressure over the droplet surface, inferred from the retardation of evaporation, would indicate a lowering of the dewpoint. To determine such an effect, we built an apparatus to provide a temperature-controlled smooth surface in the freezer. An antifreeze solution was pumped from a separate refrigerator through a dewpoint hygrometer consisting of a polished

metal container, which was held in the lower part of the freezer. By controlling the antifreeze solution flow rate, we were able to lower the temperature of the polished surface gradually to about -20°C .

With 50 μl of dimethyldichlorosilane in the cloud and the freezer temperature at 1°C , a condensed water film formed when the temperature of the smooth surface reached -7°C . With the freezer at -6°C , and 50 μl of dimethyldichlorosilane in the cloud, the smooth surface temperature was lowered from -5 to -14°C before the water began collecting. Dewpoint depression results with this method are summarized in table 2.

In another test of dewpoint lowering, about 1 ml of methyltrichlorosilane was added to the water in a half-full 1-gal bottle. Measurements with a dewpoint measuring apparatus showed a dewpoint of 18.5°C over the silane and water mixture when the dewpoint over pure water was 24°C . In another trial the dewpoint over the silane-water mixture was 7.5°C , and over pure water 13°C . Thus, in both these room-temperature trials the dewpoint lowering was 5.5°C .

2.3 Effect on Condensation Nuclei

The effect of dimethyldichlorosilane upon condensation nuclei

was investigated with the test chamber at -18°C . The chamber was open to room air and contained approximately 4000 nuclei ml^{-1} active in a thermal diffusion chamber at 1 percent water supersaturation. When 50 μl of dimethyldichlorosilane was added to the chamber, the number of condensation nuclei active at 1 percent water supersaturation increased by about 10,000 nuclei ml^{-1} .

Table 2. Dewpoint depression in silane-treated clouds

Cloud treatment	Observed dewpoint ($^{\circ}\text{C}$)	Freezer temp. ($^{\circ}\text{C}$)	Difference ($^{\circ}\text{C}$)
None	4	7	3
None	-3	-1	2
50 μl Me_3SiCl	-12	-7	5
50 μl Me_2SiCl_2	-7	1	8
50 μl Me_2SiCl_2	-14	-6	8
50 μl Me_2SiCl_2	-16	-8	8
50 μl Me_2SiCl_2	-23	-16	7
50 μl MeSiCl_3	-9	1	10
50 μl $n\text{-BuSiCl}_3$	-14	-8	6

The silane apparently reacted with the water vapor in the chamber, and the result was the formation of condensation nuclei in addition to those already present. After a few minutes, the droplets became visible within the chamber, and a stable cloud was generated. Since the vapor pressure over these nuclei surfaces was lower than for the chamber walls, droplets would grow within these condensation nuclei until their size was such that the cloud stabilized. These condensation nuclei would effect a transfer of vapor from cloud droplets that had no silane surface, or a surface imperfectly coated with silane, until equilibrium had been established between the growth of the condensation nuclei and the evaporation of untreated or imperfectly treated cloud droplets.

2.4 Effect on Ice Nuclei

The silanes that are active in cloud stabilization are also effective in modifying or preventing ice crystal growth within a supercooled cloud.

Homogeneous ice nucleation can be produced in a supercooled cloud by adiabatic expansion and cooling to below the critical temperature of -38.9°C resulting from the bursting of a small plastic bubble. This is the "pop gun effect" first noted by Vonnegut (Langmuir et al., 1948) and later discussed by Langmuir (1953).

Homogeneous ice nucleation can also be effected by the use of dry ice, which lowers the air temperature close to the dry ice surface to -78.5°C .

Silane treatment of a supercooled cloud does not interfere with the homogeneous ice nucleation process, but it does interfere with the growth of the embryonic ice nuclei, because of the reduction of the dewpoint temperature, or saturated water vapor pressure, within a silane-treated cloud.

In an untreated cloud, homogeneous ice nuclei formed either by adiabatic expansion or by seeding with dry ice can cause ice crystals to grow when the cloud is -5°C or warmer.

As noted in section 2.2, the effect on saturation water vapor pressure of a water surface treated with methyltrichlorosilane was reduction in the pressure equivalent to cooling the water by 5.5°C . This same effect of dewpoint depression was found when a supercooled cloud was treated with dimethyldichlorosilane. In the treated cloud, neither adiabatic expansion nor dry ice seeding resulted in ice crystals until the cloud temperature was lowered at least to -30°C . A very few ice crystals were observed when dry ice was used at -30°C ; a silane-treated cloud at -35°C formed large numbers of crystals when homogeneously nucleated, although

comparative visual observations indicate that the growth process is slower in the treated than in an untreated cloud.

An examination of some values of the saturation water vapor pressures over water and ice may explain the different behavior at this low temperature. The saturation vapor pressures over untreated water and ice, respectively, are 0.8070 and 0.6323 mb at -25°C , 0.5088 and 0.3798 mb at -30°C , and 0.3139 and 0.2233 mb at -35°C . If we assume a dewpoint depression of 3°C in a silane-treated cloud, the saturation vapor pressure over the water at -25°C , -30°C , and -35°C would be 0.6134, 0.3818, and 0.2323 mb, respectively. At -25°C the saturation vapor pressure would thus be less over water than over ice; at -30°C the water and ice vapor pressures would be nearly equal, with that over ice slightly lower; and at -35°C the saturation vapor pressure over ice would be significantly lower than over water. If the dewpoint depression in a silane-treated cloud were less than 3°C , the temperature at which ice crystals would begin to grow would be higher than -30°C ; if the dewpoint depression were more than 3°C , the temperature of beginning crystal growth would be lower than -30°C .

More significantly, the heterogeneous nucleation of PbI_2 and AgI in triggering ice crystals was greatly inhibited in the presence of silanes.

A threshold level was determined for the poisoning of ice crystal nuclei by silanes. Paper impregnated with AgI was burned in the laboratory to provide a supply of nuclei, and the freezer air was exchanged for room air. We then evaporated 50 μl of dimethyldichlorosilane from a warm watch glass held in the lower part of the freezer and built a cloud in the box. At this time an NCAR ice nuclei counter showed about 800 nuclei l^{-1} , but no crystals formed in the cloud, demonstrating complete deactivation. The process was repeated with 10 μl of dimethyldichlorosilane being evaporated and a count of about 600 nuclei l^{-1} . This time ice crystals formed and settled out, but an appreciable water droplet cloud remained. Under these conditions, therefore, a threshold of 10 μl of dimethyldichlorosilane for the sample cloud at -20°C was established. The process was repeated with 15 μl of the silane at -19°C , and then with 10 μl at -18°C . The nuclei counts were about 500 l^{-1} for both of these trials. Complete deactivation was produced by the 15 μl addition, and the 10 μl addition again produced partial deactivation. Before and after this series of tests, control clouds were tested without the presence of a silane. They were converted completely to ice crystals, which dropped out, removing the cloud.

It is interesting to note that complete deactivation of the AgI ice nuclei was accomplished by 15 μ l of dimethyldichlorosilane. This is less than one-fortieth of the amount needed to completely react with the water vapor at saturation over ice that is present in the chamber at -18°C , before the cloud is added.

Diphenylsilanediol evaporated in the freezer in the presence of a cloud and AgI ice nuclei did not deactivate the ice nuclei.

3. DISCUSSION

We speculate that the bonding angle of oxygen permits the polymer to have a "layered" structure (fig. 1) when the reaction takes place at the water's surface, with one side being hydrophobic because of the methyl or other organic groups. The other side would be capable of hydrogen bonding with the water surface. When a volatile chlorosilane is released within a cloud of water droplets, the reaction taking place at the surface of the droplets forms a film that lowers the vapor pressure around the droplet.

When the reaction takes place in the vapor phase the product would consist of smaller polymeric fragments which would not be

likely to become attached to a liquid water surface. Thus, the effectiveness of a unit of silane would be reduced in proportion to the fraction participating in a vapor phase reaction. This is demonstrated by comparison tests where (1) the silane was evaporated within a cloud being built, or (2) the silane was evaporated in the freezer just before the building of the cloud, with an interval of about 1/2 min during which only a vapor phase reaction could occur. For a given amount of silane, the stability of the cloud was approximately 50 percent greater in the first case than in the second.

We observed that during the life of a treated cloud the thinning is more rapid within the first 10 or 12 min and that almost a stable condition is achieved after that. Also, the average droplet size decreased, but the droplets remained visible to the unaided eye for as long as 1 hr. As we mentioned earlier, part of the thinning is due to fallout, but part can also be attributed to evaporation of the droplets. Evaporation would take place at a decreasing rate as the film would become thicker over the decreasing surface area. For example, a loss of one-half the volume of liquid water would result in a one-third reduction of surface area, producing a 60 percent increase in thickness of the silicone barrier.

Based on the tests conducted in this laboratory, the use of silanes for cloud stabilization would probably not be practical. The lowest rate of application tested, $1.0 \mu\text{l}$ for the usual sample cloud at -16°C extended the life of the cloud by a factor of four or five, but during this time there was considerable thinning. At this rate of application, a cloud containing 1 g of liquid water per cubic meter and occupying 0.1 km^3 would require 10^2 liters of silane. At higher temperatures the efficiency would be lower because of the greater quantity of water vapor present, e. g., at 5°C there would be about five times as much water vapor in the same volume. However, in a natural cloud the wall effect of the test chamber would not be present, and because of this the stabilization efficiency could be much greater.

4. ACKNOWLEDGEMENT

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