Photoinduced Nucleation of Water Vapor

Abstract. *Strong photoinduced nucleation of pure water vapor was found to occur in a wavelength range where no ultraviolet absorption of water vapor has been reported. Systematic studies were made of the dependence of the nucleation rate and the delay time for the initiation of nucleation on light intensity. The results obtained were accurately fitted by a phenomenological mechanism whereby the nucleation is initiated by clusters accumulating an appropriate number of photoexcited water molecules.*

We recently reported (*1*) that photoinduced nucleation occurred when a supersaturated nonane vapor phase containing low concentrations of *o*-tolualdehyde was irradiated with ultraviolet light of suitable wavelength and intensity (*2*). Although light (over the wavelength range and up to the maximum intensity we have available) has no nucleating effect on pure ethanol, pure heptane, or pure nonane (*3*), it does cause photoinduced nucleation in certain other pure substances (water, benzene, toluene, *o*-xylene, and carbon tetrachloride). We report here on systematic studies of this effect in the most interesting of these pure substances, water.

We have studied both supersaturated pure water vapor and low concentrations of water in supersaturated ethanol vapor. We find that (i) photoinduced nucleation is an intrinsic property of water and is not due to an impurity as has been previously supposed (*4*), (ii) it occurs from 200 to 320 nm, a wavelength range where no ultraviolet absorption of water vapor has been observed (*5*), (iii) it can occur at extremely low supersaturations, and (iv) it occurs by a different mechanism from that which fitted the photoinduced nucleation measurements on *o*-tolualdehyde in nonane.

The setup and the operation of the thermal diffusion cloud chamber and the light source used in the present studies are the same as those used in our earlier experiments (*1*). Since the molecular weight of water is so small, for most of these studies H_2 was used as the carrier gas instead of He to minimize possible convection problems.

We measured the nucleation spectrum, that is, the light intensity required to cause a given steady-state rate of nucleation as a function of wavelength. (For these measurements the cloud chamber was maintained at a steady state such that the maximum supersaturation anywhere in it was always lower than that required for homogeneous nucleation to occur.) Upon irradiation with light of suitable wavelength and intensity, after some seconds of delay, nucleation commences and rises to a constant rate. Once the light has been turned off, the nucleation can still be observed to occur for a period of 10 to 300 seconds. The wavelength dependence of the light intensity required to obtain a nucleation rate of two drops per square centimeter per second is shown in Fig. 1 (*6*).

We also carried out studies on the effect of supersaturation. As the supersaturation decreased, the same general dependence of intensity on wavelength was maintained (see Fig. 1). Decreasing the supersaturation increased the amount of light required. At the maximum light intensity (about 0.2 W m^{-2}) available from our light source at 200 nm (the wavelength where the photoinduced nucleation effect is strongest), we were able to detect photoinduced nucleation of pure water at supersaturations as low as 1.00042 (that is, at a relative humidity of 100.042 percent).

We have also studied the nucleation spectrum of water in a supersaturated ethanol vapor phase. (In these experiments, we repeatedly verified that, in the absence of water, the pure ethanol vapor does not photonucleate at any supersaturation, light wavelength, or light intensity.) We were able to observe photoinduced nucleation at water concentrations as low as 1000 parts per million (ppm) by volume in the liquid phase. The result for 1 percent water in ethanol is also shown in Fig. 1.

Some effects related to the photoinduced nucleation of water vapor have been observed. Clark and Noxon (*7*) reported that in the photolysis of water vapor at wavelengths between 150 and 170 nm a cloud containing about 10^4 particles per cubic centimeter of micrometer size with low density (0.2 g cm^{-3}) and unit positive charge was produced even when the water vapor was undersaturated. Reiss *et al.* (*4*) were the first to report photoinduced nucleation of water at higher wavelength. They observed it in their thermal diffusion cloud chamber experiments with ultraviolet light of wavelengths less than 250 nm. They concluded that the nucleation was not caused by the formation of ions since an electric field did not affect the nucleation rate. However, from the results they observed at various total pressures, they suggested that the nucleation was due to the polymerization of a trace impurity in the carrier gas. One might therefore attribute photoinduced nucleation to uncontrolled photochemistry associated with trace impurities, thus causing formation of products of very low volatility which then serve as condensation nuclei. We paid particular attention to this possibility in our experiments.

We have found that doubly and triply distilled water samples from two sources (well water and river water) and water that was doubly distilled, then distilled over $KMnO_4$, and then redistilled at least twice all exhibited identical nucleation spectra. The same spectra were also produced with the use of either He or H_2 as the carrier gases. Since these carrier gases did not induce nucleation in either pure nonane or pure ethanol and had identical effects on water, we think it safe to conclude that the nucleation was not due to impurities in the carrier gas.

Because of its high surface tension, water does not wet the metal surface of the cold plate very well. As a result, large drops form which fall through the chamber to the liquid pool, disturbing to some extent the steady-state operating condition. The roughness of the liquid-vapor interface at the cold plate also makes the calculation of the super-

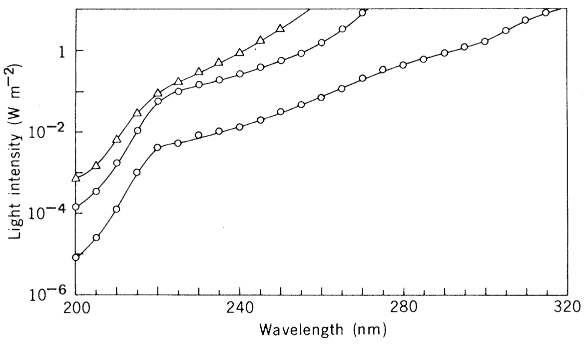

Fig. 1. The light intensity required to cause a nucleation rate of two drops per square centimeter per second as a function of wavelength. The bottom curve shows the results obtained from experiments with pure water vapor at a supersaturation $S = 3.059$ at 295.44 K. The middle curve shows the results obtained at a lower supersaturation, $S = 2.257$, at 302.34 K. The top curve shows the results obtained for 1 percent water in ethanol at an ethanol vapor supersaturation $S = 1.775$ at 284.40 K.

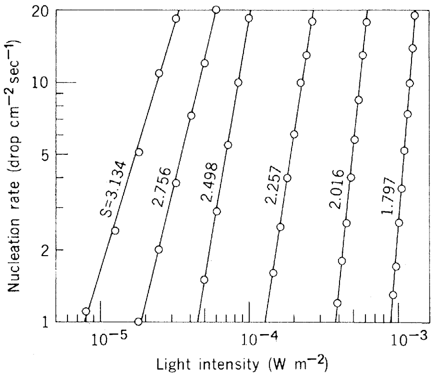

Fig. 2. The steady-state nucleation rate of pure water vapor as a function of light intensity at a wavelength of 200 nm at different constant supersaturations, S.

saturations inside the chamber somewhat uncertain. By covering the cold plate surface with a clean Kimwipe, a very thin (0.075 mm) cellulose fiber sheet, we were able to completely eliminate the wetting problem and a satisfactorily thin film of liquid was formed. In order to verify that the Kimwipe was free from volatile impurities which might cause photoinduced nucleation in the vapor, with the same Kimwipe sheet in place the chamber was evacuated and drained and fresh pure water and pure H_2 were introduced many times, each introduction being made after several hours of steady-state operation. The spectra measured after each introduction remained identical. We obtained further proof that the Kimwipe had no nucleating effect by comparing the nucleation spectrum obtained in experiments made using it to those obtained in a carefully cleaned chamber using only pure water; identical results were always obtained.

Gas chromatographic analysis of water samples taken from the cloud chamber both before and after the experiments showed no peaks other than those of pure water. Thus, impurities, if there were any, had to be present in concentrations lower than about 1 ppm. Since the light intensity required to cause a nucleation rate of about two drops per square centimeter per second in water at its most effective photonucleating wavelength (200 nm) is about 1/10 of that required for 1000 ppm of *o*-tolualdehyde in liquid nonane at its most effective photonucleating wavelength (242 nm), it is highly unlikely that any impurity at concentrations less than 1 ppm could have such a strong effect. Furthermore, if the photoinduced nucleation that we observed at a supersaturation of 1.00042 were due to an impurity, the impurity nucleus would have to contain 10^{12} molecules or more (if the nucleation were to be caused by ordinary heterogeneous nucleation).

We are certain that the nucleation is not due to the formation of ions for the following reasons. (i) An electric field as strong as 200 V cm^{-1} has no effect on the observed rates of nucleation. (ii) Photoinduced nucleation is observed to occur at supersaturations much smaller than those that, as we have measured, are required for nucleation on ions.

Deliberate introduction of 5 torr of O^2 into the chamber produced no change in nucleation spectra, even after several hours of irradiation with ultraviolet light. This observation tends to exclude as the cause of the nucleation a number of radicals and other molecules that are commonly formed from O_2 in the presence of strong ultraviolet light. Furthermore, although we have not compared the absorption spectra for all such species (for example, O_3, OH, H_2O_2, HO_3, and others) with our nucleation spectrum, we were able to find a spectrum for H_2O_2 (*8*) and found no correlation.

We measured the steady-state nucleation rates and the delay times for the start of nucleation after the light was turned on as functions of light intensity at several different supersaturations. Table 1 shows the values of α and β, which are, respectively, the slopes of the straight lines obtained from Figs. 2 and 3, that is, the log-log plots of the nucleation rate and the delay time versus light intensity at different supersaturations. These measurements were made at a light wavelength of 200 nm and a total pressure of 800 torr (we obtained the various supersaturations by maintaining the temperature of the surface of the liquid pool constant at about 337 K while varying the cold plate temperature). Also shown in Table 1 are the maximum supersaturations (S) in the cloud chamber and the temperatures (T) corresponding to these maximum supersaturations.

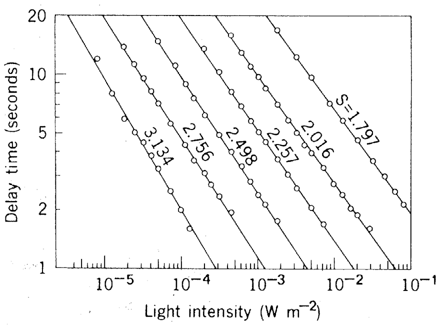

Fig. 3. The delay time for the start of the nucleation of pure water vapor as a function of light intensity at a wavelength of 200 nm at different constant supersaturations, S.

Table 1. Values of α and β, the slopes of the plots (Figs. 2 and 3) of the nucleation rate and the delay time versus the light intensity at various maximum supersaturations, S. Also shown are the temperature, T, at that maximum supersaturation, and c, the number of excited water molecules in the cluster as calculated from α and β by means of Eqs. 6 and 7. The ranges for the possible values of c due to the uncertainties (1 standard deviation) in α and β are shown in parentheses.

S	T (K)	α	β	c (from nucleation rate data)	c (from delay time data)
3.134	295.06	2.05 ± 0.07	−0.698 ± 0.013	2.05 (1.98–2.12)	1.76 (1.69–1.85)
2.756	297.53	2.51 ± 0.07	−0.620 ± 0.006	2.51 (2.43–2.58)	2.58 (2.48–2.69)
2.498	300.29	3.63 ± 0.09	−0.593 ± 0.007	3.63 (3.54–3.72)	3.19 (3.00–3.41)
2.257	302.34	3.91 ± 0.14	−0.565 ± 0.007	3.91 (3.77–4.05)	4.35 (3.97–4.81)
2.016	306.07	6.07 ± 0.12	−0.550 ± 0.004	6.07 (5.95–6.19)	5.50 (5.13–5.94)
1.797	309.42	7.94 ± 0.15	−0.531 ± 0.004	7.94 (7.79–8.09)	8.57 (7.64–9.76)

We found that it was not necessary to invoke the phenomenological mechanism of two photons to form the initiator and one photon to form the propagator as was the case in the *o*-tolualdehyde experiments (*1*). In fact, this mechanism did not fit the results obtained for water. Instead, a different phenomenological mechanism, a simple clustering of excited molecules, accurately fits our experimental values of α and β. This mechanism is

$$H_2O \xrightarrow{m\,h\nu} (H_2O^*) \quad (1)$$

$$(H_2O^*) + (H_2O^*) \rightarrow (H_2O^*)_2 \quad (2)$$

$$\vdots \qquad \vdots \qquad \vdots$$

$$(H_2O^*)_{c-1} + (H_2O^*) \rightarrow (H_2O^*)_c \quad (3)$$

where $(H_2O^*)_c$ represents the cluster which has acquired c excited water molecules (and an undetermined number of unexcited water molecules). This mechanism suggests that, on irradiation with light ($h\nu$) of a given wavelength and intensity, a few water molecules in the vapor are excited into a higher energy state. During the clustering process in a supersaturated vapor phase, these photoexcited molecules may be incorporated, along with an undetermined number of unexcited molecules, into clusters. When a cluster accumulates c excited molecules, these excited molecules can cause the cluster to serve as a condensation nucleus for the formation of a visible droplet.

The differential equations describing the dependence of the concentrations of the various-sized clusters on time, water vapor concentration, and light intensity can be readily solved in two limiting cases, an initial time solution and a steady-state solution. (These are precisely the solutions we need for comparison with the delay time data and the steady-state nucleation data, respectively.) In both cases we make the reasonable approximation that the concentrations of the clusters rapidly decrease with increasing size. For the initial time solution we also neglect diffusional losses and obtain for the concentration of c-sized clusters

$$[(H_2O^*)_c] = K_c[H_2O]^{cm}\, I^{cm}\, t^{c(p+1)-1} \quad (4)$$

where K_c is a constant, m is the number of photons needed to excite a water molecule, I is the light intensity, t is time, and p is the number of substeps involved in the initial excitation process. For the steady-state solution we do not neglect the diffusional losses. Instead, we assume that they are the dominant loss mechanism and thus obtain

$$[(H_2O^*)_c] = K'_c[H_2O]^{cm}\, I^{cm} \quad (5)$$

where K'_c is a different constant. If there is a unique number c which can cause nucleation at a given supersaturation condition and if the rate of nucleation is proportional to $[(H_2O^*)_c]$, it follows that

$$\alpha = cm \quad (6)$$

$$\beta = -cm/[c(p+1)-1] \quad (7)$$

The values of α and β in Table 1 were obtained by a least-squares fit of the data in Figs. 2 and 3 and also their uncertainties (1 standard deviation). To obtain the same value of c from the α and β data using Eqs. 6 and 7 (to within the uncertainty in c due to the uncertainties in α and β), we were forced to require that $m = 1$ and $p = 1$. (These are precisely the values one would choose on physical grounds; that is, one photon is required to excite water and this excitation occurs in a one-step process.) No other model (for example, the one that fits the *o*-tolualdehyde data) would produce the same value of c for both the steady-state rate data and the delay time data for any value of the parameters.

Although the above mechanism fits our steady-state nucleation rate and delay time data very well, some questions about the fundamental causes of the photoinduced nucleation phenomenon remain to be answered:

1) Presumably the light has to be absorbed to be effective. However, there is no known absorption by H_2O in the wavelength range from 200 to 320 nm.

2) In this wavelength range, photoexcited molecules typically undergo electronic transitions. The lifetimes of electronic excited states are generally short (submicroseconds to milliseconds). This is difficult to reconcile with our observations that it takes seconds to minutes for nucleation to begin after the light is turned on and to cease after the light is turned off.

3) All current theories of nucleation view the process as occurring by a balance of molecules arriving at and evaporating from the clusters. If the energy of the photoexcited molecules were to be degraded to heat, then its effect (if the excited molecules were actually in clusters, which is what the phenomenological mechanism suggests is the case) would be to increase the evaporation rate. Such an effect would prevent nucleation and not promote it.

These questions force us to the following conclusions. (i) There must be absorption of light over the wavelength range we studied. However, these absorptions are probably very weak and are not readily detectable by other means. (ii) Either the lifetimes of the photoexcited molecules are greatly extended by their interaction with the other excited and the unexcited molecules in the cluster or some kind of photochemistry (for example, radical formation or polymerization) is going on. (iii) It is unclear how a cluster of excited molecules can cause other molecules to condense on it.

The photoinduced nucleation phenomenon we have observed using *o*-tolualdehyde in nonane, pure water vapor, and other substances has several important implications. Its distinctive wavelength dependence can be utilized to detect and identify substances even when they are present in very low concentrations. The observance of an effect at wavelengths where no absorptions have been reported may mean that one now has a new and more sensitive tool for detecting such absorptions. Since the conditions we used in our cloud chamber are comparable to those found in the atmosphere (*9*), the photoinduced nucleation of water vapor may be an important mechanism for cloud formation. The light-sensitive organic substances we studied (*2*) are common photoactive pollutants found in urban atmospheres (*10*). Our study thus suggests that the photochemical aerosol formation mechanism may be due to photoinduced nucleation and not to self-nucleation mechanism as has been suggested (*11*).

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References and Notes

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12. We thank Dr. R. Partch for carrying out the chemical analysis of the water samples. This research was supported under grant ENG72-04041 A02 from the National Science Foundation.

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The Oldest Bryozoans: New Evidence from the Early Ordovician

Abstract. *An abundant, previously problematic fossil from the Lower Ordovician (Canadian) Black Rock limestone of the Ozark Uplift area is an undescribed dianulitid bryozoan. It is believed to be the oldest unquestionable bryozoan known. The growth morphology varies widely and is believed to be environmentally influenced.*

Bryozoans older than earliest Middle Ordovician in age (Whiterockian Stage) (*1*) have never been recognized with certainty from the fossil record. Previous finds of older forms are of questionable affinities (*2*) or of uncertain stratigraphic position (*3*). The recognition of a previously problematic fossil from the Lower Ordovician (late Canadian) Black Rock limestone (*4*) of northeastern Arkansas and southeastern Missouri as an undescribed dianulitid species is believed to mark the oldest known occurrence of an unquestionable bryozoan.

Fossils from the Black Rock limestone of northeastern Arkansas were suspect-

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