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17 December 1976

Nucleation on Photoexcited Molecules

Abstract. *On irradiation with light of suitable wavelength and intensity, certain organic compounds, even at very low concentrations, cause very efficient nucleation of supersaturated vapors. A mechanism is suggested to account for this phenomenon. Nuclei containing only a few photoexcited molecules are responsible for the nucleation.*

In a paper presenting results on the homogeneous nucleation of *n*-alkyl benzenes (*1*), Katz *et al.* reported that light of wavelength shorter than 420 nm caused marked increases in the observed rates of nucleation. We have now determined that the light-induced nucleation was probably due to the contamination of the alkyl benzenes by very small amounts of *o*-alkylbenzaldehydes (*2*). This report describes studies on the nucleation of liquid droplets from a supersaturated vapor phase caused by irradiation with light of suitable wavelength when this vapor phase contains trace amounts of certain organic substances. On the basis of careful observations, we have determined that (i) this nucleation is not a homogeneous nucleation process, (ii) the nucleation center is not charged, (iii) this nucleation is not a heterogeneous nucleation process in the ordinary sense, and (iv) the nucleation is not caused by dust particles or other artifacts. In short, this phenomenon cannot be explained by existing nucleation theories.

The thermal diffusion cloud chamber employed in this nucleation study has been developed and used in this laboratory for many years (*1, 3, 4*) for the study of the condensation of liquid drops from the vapor phase. The chamber is designed so that one-dimensional diffusion takes place through a gas of low molecular weight, usually helium, from a hotter to a cooler plate. The bottom plate is covered by a shallow liquid pool of a nucleating substance doped with a low concentration [typically 0.1 to 100 parts per million (ppm)] of the light-sensitive organic substance under investigation. The vapors evaporate from the surface of the liquid pool, diffuse upward, condense on the upper plate (which is slightly conical), flow to its edge, and return to the liquid pool by way of the chamber wall. The temperature, partial pressure, and thus the supersaturation of nucleating vapor inside the chamber are well defined and are obtained by solving the heat and mass flux equations (*1, 3*). At sufficiently large supersaturations, homogeneous nucleation occurs; small droplets can be readily observed to form and fall to the lower plate. At slightly lower supersaturations, no droplet formation whatever is observed (*5*). However, upon irradiation with light of suitable wavelength and intensity, after a brief delay (1 to 30 seconds), nucleation commences and rapidly rises to a constant rate (*6*) even at supersaturations much too low to cause homogeneous nucleation (or even nucleation on ions). Once the light has been turned off, the rate of nucleation decreases to zero over a period of 20 to 300 seconds.

We have investigated the effects of supersaturation, the concentration of the light-sensitive organic substance, the wavelength and the intensity of the light, and the irradiation time on the rate of nucleation. A quartz-ringed thermal diffusion cloud chamber with a 1000-watt xenon light source and a 0.25-m monochromator was used (yielding a maximum light intensity for 10-nm resolution of about 10 watt m^{-2} at 400 nm). The cloud chamber was set to a steady state, with a light-insensitive nucleating vapor which is supersaturated. Carefully purified samples of heptane and nonane were used. For each of these substances we verified that, in the absence of the nucleating dopant, no light effect at any supersaturation, light wavelength, or light intensity was observable. Initial studies of the dopants *o*-tolualdehye, *p*-tolualdehyde, crotonaldehyde, benzoic acid, and *o*-nitrotoluene have shown that they all induce nucleation upon irradiation, with a relative nucleation efficiency which varies strongly from compound to compound and very strongly with wavelength.

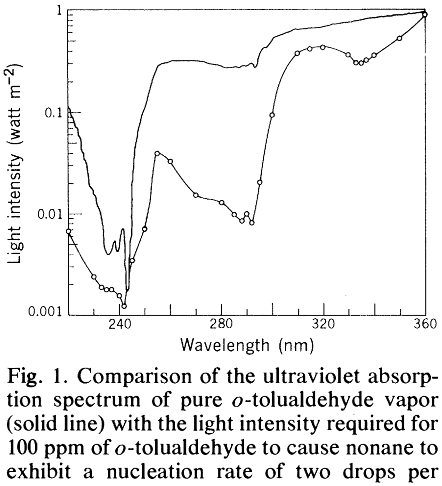

Fig. 1. Comparison of the ultraviolet absorption spectrum of pure *o*-tolualdehyde vapor (solid line) with the light intensity required for 100 ppm of *o*-tolualdehyde to cause nonane to exhibit a nucleation rate of two drops per square centimeter per second at a supersaturation $S = 7.249$ at 290.99 K (solid line with open circles).

Systematic studies have been carried out on *o*-tolualdehyde in nonane at one concentration (100 ppm by weight) (*7*). No light effect was observed at wavelengths longer than 400 nm. From 400 nm to about 300 nm there is a definite nucleating effect with a peak at 335 nm and a minimum at 320 nm. The light effect then increases very strongly, reaching two peaks in the range 285 to 295 nm. It decreases somewhat and then reaches another strong peak at about 242 nm (*8*). In principle, one would like to determine the rates of nucleation as a function of wavelength at constant intensity; however, these rates can be reliably determined over only a limited range (about 0.2 to 100 drops crossing 1 cm^{-2} sec^{-1}) because of fluctuation effects at low rates and depletion of the nucleating material (for example, the nonane) at high rates. Since, at constant light intensity, the change in the rate of nucleation as a function of wavelength is much wider than this range, we were forced to change the light intensity. Studies at several wavelengths showed approximately the same dependence of the rate of nucleation on intensity. Thus, a study of the intensity required to obtain the same rate of nucleation as a function of wavelength is roughly reciprocally equivalent to a study of the rate as a function of wavelength at constant intensity. Superposing (see Fig. 1) a vapor-phase ultraviolet absorption spectrum of pure *o*-tolualdehyde on a plot of wavelength as a function of the light intensity required to cause a given rate of nucleation, one sees significant correlation. The peaks in the region 285 to 295 nm correspond to a weak vapor-phase absorption in the pure aldehyde which is due to a n-π^* transition. The 242-nm peak corresponds to a much stronger π-π^* transition.

We have studied the steady-state nu-

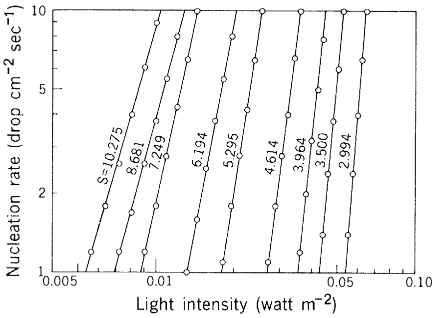

Fig. 2. The nucleation rate as a function of light intensity at a wavelength of 290 nm at different constant supersaturations, S.

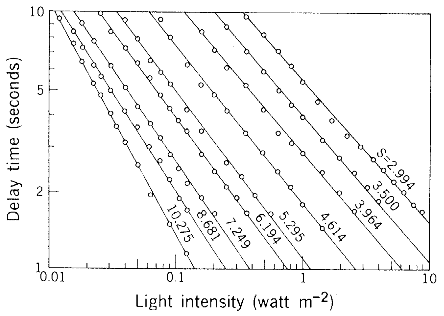

Fig. 3. The delay time as a function of light intensity at a wavelength of 290 nm at different constant supersaturations, S.

cleation rates and the delay times for the start of nucleation after the light was turned on as functions of light intensity at several nonane supersaturations. The dependence of the rate of nucleation (J) and of the delay time ($\bar{t}$) on light intensity (I) can be fitted by the equations

$$J = K_1 I^\alpha \tag{1a}$$

and

$$\bar{t} = K_2 I^\beta \tag{1b}$$

where K_1 and K_2 are constants. In Table 1 are given the values of α and β which are the slopes of the straight lines shown in Figs. 2 and 3, that is, the log-log plots of J and $\bar{t}$ versus light intensity. The data in Figs. 2 and 3 and Table 1 are for measurements made at a wavelength of 290 nm and a total pressure of 800 torr; we used nonane containing 100 ppm of *o*-tolualdehyde at various supersaturation conditions obtained by holding the temperature of the surface of the liquid pool constant at about 352 K while varying the cold plate temperature (*9*). Also shown in Table 1 are the maximum supersaturations (S) in the cloud chamber and the temperatures (T) corresponding to these maximum supersaturations. Note that the lowest of these supersaturations is very much smaller than that required to cause homogeneous nucleation or nucleation on ions. Strong light-induced nucleation was still observable at much lower supersaturations than those listed in Table 1; for example, at $S = 1.118$ and $T = 341.34$ K, a rate of nucleation of about 100 drops falling through 1 cm^{-2} sec^{-1} was generated for a light intensity of about 1.5 watt m^{-2}. We did not attempt to obtain the rate and the delay time correlations at these lower supersaturations since the nucleation was not uniformly distributed in the pathway of the light beam in the chamber.

Although nucleation phenomena have been extensively studied in recent years, no existing theory can be used to explain our observations. Ions will cause nucleation at slightly lower supersaturations than those required for homogeneous nucleation, but the supersaturation lowerings obtained here are much larger. Furthermore, an electric field was found to cause no difference in the nucleation rate; this result implies that the nucleation centers are not electrically charged. Heterogeneous nucleation, in the ordinary sense, requires quite large nucleation centers. For example, at $S = 1.118$ and $T = 341.34$ K, the nucleation center, consisting of active species and nonane molecules, should contain about 138,860 molecules (the number will be about 138,860 for perfect wetting and larger for imperfect wetting, and the active species should contribute a major portion of the volume to become effective). Since in our case the partial pressure of the active species is at most of the order of 10^{-7} torr, on the basis of simple kinetic theory it is unlikely that enough molecules of the active species can accumulate, with nucleating vapor molecules, into such large nucleation centers in the observed delay time of about 30 seconds.

While the detailed mechanisms for the formation of such efficient nucleation centers are not yet known, a tentative mechanism which fits the values of both α and β (Table 1) is the following. Light ($h\nu$) at a given wavelength excites the *o*-tolualdehyde molecules into two different states. The first state is sufficiently energetic to serve as an initiator but is present only in low concentration; the second, present in higher concentration, can serve only as a source of active monomers for the growing clusters, that is,

$$\text{aldehyde} \xrightarrow{n\,h\nu} \text{A}^* \tag{2}$$

$$\text{aldehyde} \xrightarrow{m\,h\nu} \text{In}^* \tag{3}$$

$$\text{In}^* + c\,\text{A}^* \longrightarrow \text{In}^* - (\text{A}^*)_c \tag{4}$$

where In*, A*, and In* − (A*)$_c$ represent, respectively, the initiator, the excited aldehyde, and the cluster containing $c + 1$ aldehydes (one initiator plus c aldehydes). When the cluster is large enough to serve as a nucleus, nonane condenses on it and a visible droplet is formed and counted. If the concentrations of initiator and of excited aldehyde are given by $[\text{A}^*] \propto I^n t^q$ and $[\text{In}^*] \propto I^m t^p$, respectively, and if

$$[\text{A}^*] \gg [\text{In}^* - \text{A}^*] \gg \cdots \gg [\text{In}^* - (\text{A}^*)_{c-1}] \gg [\text{In}^* - (\text{A}^*)_c]$$

we obtain for the concentration of clusters containing $c + 1$ aldehydes

$$[\text{In}^* - (\text{A}^*)_c] = K_c I^{m + cn} t^{p + c(q + 1)} \tag{5}$$

where K_c is a kinetic constant that depends on [In*], [A*], and c. Assuming that there is a unique size c which may cause nucleation under a given set of conditions, Eq. 5 is of the form of Eq. 1 with

$$\alpha = m + cn \tag{6a}$$

and

$$\beta = -(m + cn)/[p + c(q + 1)] \tag{6b}$$

The experimental data for α and β restrict our selection of m, p, n, and q to only one set of values with $m = 2$, $p = 1$ and $n = 1$, $q = 1$. This limitation suggests that the initiator is formed by a two-photon process, and that one photon

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 aldehyde molecules in the cluster as calculated from α and β by means of Eq. 6.

S	T (K)	α	β	c (from nucleation rate data)	c (from delay time data)
10.275	284.75	3.44	−0.909	1.44	1.33
8.681	287.09	3.83	−0.788	1.83	2.10
7.249	290.99	4.63	−0.725	2.63	2.83
6.194	293.38	5.41	−0.669	3.41	3.94
5.295	296.98	6.45	−0.650	4.45	4.50
4.614	299.18	8.13	−0.610	6.13	6.32
3.964	302.82	9.80	−0.582	7.80	8.65
3.500	305.17	11.10	−0.572	9.10	9.92
2.994	309.13	13.33	−0.551	11.33	14.20

creates an A* and that the excited aldehydes are so long-lived that they accumulate (*10*). With this set of values, one obtains approximately the same values for c for both the rate and the delay time studies at each supersaturation (see Table 1). Surprisingly, c is very near to unity at high supersaturation, for example, $S = 10.275$ and $T = 284.75$ K and increases to only about 14 at $S = 2.994$ and $T = 309.13$ K. These values of c ($c \sim 1$ and $c \sim 14$) are very much smaller than the minimum number of molecules required for a nucleation center for ordinary heterogeneous nucleation (about 50 and 290 molecules, respectively, if nonane wetted the cluster perfectly). At present, we have no detailed explanation for why clusters of these photoexcited molecules at sizes so much smaller than those required for the homogeneous nucleation of nonane are so efficient at causing nucleation. In some as yet undetermined fashion, the excess energy available in these molecules promotes the formation of nonane clusters.

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5. The chamber is self-cleaning since any dust or other foreign nuclei present in it will cause nucleation; under these circumstances a droplet will form and fall into the liquid pool where the nucleus will be trapped by surface forces.
6. Since the vapors keep diffusing upward, there is a residence time, depending on the supersaturation condition, in which a vapor molecule diffuses through the light beam. A constant nucleation rate is reached for an irradiation time longer than this residence time.
7. An observable effect occurs at concentrations as low as 0.01 ppm.
8. Our light source is very weak below 220 nm. Light effects below this wavelength are thus uncertain.
9. Holding the temperature of the liquid pool constant ensures that the composition of the vapor phase remains approximately constant.
10. We do not mean to imply that the actual process involves the simultaneous absorption of two photons. The light intensities we used are probably too low for this to be the significant mode of initiator generation. What probably occurs is the absorption of a second photon by an already excited aldehyde. But these two processes are indistinguishable on the basis of our present experimental methods.
11. This work was supported under NSF grant ENG 72-04041 A02.

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Polyelectrolytes: Potential Chloroform Precursors

Abstract. *Chloroform residues in potable water are generally thought to be derived only from the organic matter in the raw water upon chlorination. However, formation of chloroform at concentrations of a few micrograms per liter from widely used polyelectrolyte coagulants and coagulant aids has now been observed. Most of the ten commercial polyelectrolyte formulations tested reacted with chlorine to form chloroform under thermal conditions. This reaction was found to be strongly activated by ultraviolet irradiation. Since the chemical composition of polyelectrolytes and their impurities are little known, further studies are required before a full assessment of their benefits and potential harm can be made.*

Trihalomethanes, notably chloroform, have been observed in many municipal water supplies (*1*). Their formation is generally attributed to the reaction of chlorine with the organic matter present in the raw water. Certain high-molecular-weight polymers (polyelectrolytes or PE's) are commonly used as coagulants or coagulant aids for the treatment of potable water (*2*). In practice, PE's are usually applied at concentrations of 1 to 10 mg/liter after chlorination of the raw water. At present, the analytical techniques for the determination of PE's in finished water lack sensitivity and specificity, but unreacted PE's and some breakdown products have recently been reported in potable water (*3*).

Table 1. Chloroform formation from polyelectrolyte solutions containing 10 mg/liter chlorine, under thermal and ultraviolet light–activated conditions. All values are the means of two determinations with <15 percent standard deviation and are corrected for background (*7*). Reaction time was 4 hours under thermal conditions, 1 hour under ultraviolet (UV).

Polyelectrolyte		Chloroform produced (ng/liter)	
Type	Concentration (mg/liter)	Thermal	UV
Cat-Floc	10	0.4	ND*
Cat-Floc-T	1	ND	1.5
	10	0.5	7.1
	10	1.2†	3.1†
	10	1.5†‡	ND
	10	1.1‡	ND
	100	2.4	29.2
Separan NP10	1	ND	0
	10	0	1.8
	100	ND	10.9
CA 243	1	ND	1.3
	10	0	2.4
	100	ND	17.8
Amerfloc 445	1	ND	2.7
	10	2.7	7.6
	100	ND	12.0
Drewfloc 1	1	ND	0
	10	0.4	0.8
	100	ND	1.8
Drewfloc 9125	1	ND	0.1
	10	0.5	0.5
	100	0.5	2.0
Nalcolyte 607	10	0	0
	100	ND	7.8
Nalcolyte 85016	10	0	1.8
	100	ND	22.8
Nalcolyte 5WP549	100	1.5	28.8
Nalcolyte 8101	100	ND	13.8

*ND, value not determined. †Chlorine concentration, 2 mg/liter Cl_2. ‡Reaction time, 24 hours.

We report here on the formation of chloroform from some of these commonly used PE's under experimental conditions similar to those in municipal water treatment plants. Ten commercial PE formulations (many claimed to be resistant to chlorine) were investigated under two principal chlorination conditions: (i) with thermal reaction only for periods of 4 and 24 hours, and (ii) with ultraviolet (UV) irradiation for 60 minutes. The results are summarized in Table 1.

The maximum PE concentrations recommended for potable water treatment (*1*) are usually in the range 1 to 30 mg/liter. Although an unknown percentage of the applied PE will be precipitated and removed from the water, it has been stated (*4*) that "Because of the uncertainty of the removal of polyelectrolytes in water treatment, the best practice is to consider any toxic hazard on the basis of the applied dose of chemicals." Therefore, the investigated PE concentrations of 1 to 100 mg/liter are within the realm of common treatment procedures, particularly when one considers the possibility that concentration gradients exist before complete mixing of the water and the PE solution.

The current chlorination practice for potable water varies with the quality of the raw water, and chlorine concentrations lie in the range of approximately 1 to 16 mg/liter (*5*). Therefore, the experimental chlorine concentrations, 2 and 10 mg/liter (applied as 5 percent aqueous sodium hypochlorite), are also within the usual range of conditions. The analytical procedure for chloroform determinations has been described earlier (*6*); additional experiment details are given in (*7*).

The results, as shown in Table 1, indicate very slow formation of chloroform