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.

30 August 1976; revised 11 January 1977

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 from chlorinated PE solutions under thermal conditions. After 4 hours reaction time, only slight increases of chloroform concentration above the blank value were noted. A 10 mg/liter solution of Cat-Floc-T with a reaction time of 24 hours produced $CHCl_3$ at a concentration of 1.1 μg/liter, compared to 0.5 μg/liter for a reaction time of 4 hours. Larger chloroform concentrations were observed after ultraviolet irradiation of the solution (*7*). Compared to 0.5 μg/liter $CHCl_3$ after 4 hours of thermal conditions, 7.9 μg/liter was produced after the same Cat-Floc-T solution (10 mg/liter) was irradiated for 1 hour. A similar irradiation of 100 mg/liter Cat-Floc-T resulted in the formation of 29.2 μg/liter $CHCl_3$. These and other results in Table 1 illustrate the photoenhancement of chloroform formations from commercial PE's and chlorine.

Generally, municipal water treatment plants in the northern United States and in Canada are enclosed and shielded from direct sunlight. Therefore, in these plants the thermal reaction will predominate, with only minimal formation of chloroform. In contrast, water treatment plants in which the water is exposed to sunlight, such as open-air plants in more temperate climatic zones, could derive larger amounts of chloroform from PE's by the ultraviolet pathway.

The possibility of chloroform formation from PE's was first raised in the report on the National Organics Reconnaissance Survey for Halogenated Organics in Drinking Water (*1*). It was observed that finished water from treatment plants that used PE's generally had higher total concentrations of trihalomethanes than water from plants that did not use PE's. The average trihalomethane concentration in all 80 cities surveyed was 0.5 μmole/liter (59 μg/liter if this was all present at $CHCl_3$). Sixty-three of the cities employed filtration in their treatment process, and 16 of these used PE's on a regular basis. The cities using PE's had an average trihalomethane concentration 51 percent higher than did cities which employed filtration but not PE's. One should not infer from these results that the excess chloroform is due to the PE's, as many of these cities probably had below-average raw water quality that caused them to switch to PE's in the first place. In general, there is a definite lack of information on the precise chemical composition of commercial PE formulations; their impurities, such as monomers and oligomers; and their removal with the treatment processes. More detailed studies must be undertaken before the relative contributions of PE's, or their impurities, as chloroform precursors can be assessed. Polyelectrolytes are now generally accepted as valuable coagulants for the removal of other, more abundant, potential chloroform precursors, and it may well be that their benefits outweigh any detrimental side reactions, such as that reported above.

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7. Commercially available aqueous solutions containing approximately 15 percent PE were diluted with distilled water to give 1000 mg/liter stock solutions. Portions of 10, 1, and 0.1 ml of the PE stock solution were diluted to give 100 ml each of PE solutions containing 100, 10, and 1 mg/liter in 100-ml volumetric flasks. To these, 1 or 0.2 ml of a 1000 mg/liter chlorine stock solution, prepared by dilution of a 5 percent NaOCl solution (Baker), was added. For the thermal reactions, the volumetric flasks were kept at 20°C in a dark room. For the light activation experiments, the solutions in the volumetric flasks were irradiated in a Rayonet Photochemical Reactor, model RPR-100, at a wavelength of 3500 Å. The light intensity, as measured by actimome → [C. G. Hatchard and A. C. Parker, *Proc. R. Soc. London Ser. A* **235**, 518 (1956)], was 6.3×10^{-9} einstein ml^{-1} sec^{-1}. Blank experiments for the background determination were done with distilled water and chlorine only. The chloroform concentrations observed under various conditions were as follows. Under thermal conditions and 4 hours reaction time, with 10 mg/liter Cl_2, 0.8 μg/liter $CHCl_3$; and with 2 mg/liter Cl_2, 0.4 μg/liter $CHCl_3$. Under thermal conditions and 24 hours reaction time, with 10 mg/liter Cl_2, 1.3 μg/liter $CHCl_3$; and with 2 mg/liter Cl_2, 0.8 μg/liter $CHCl_3$. Under ultraviolet irradiation for 1 hour, the background $CHCl_3$ concentrations were 0.3 and 1.2 μg/liter for Cl_2 concentrations of 2 and 10 μg/liter, respectively.

25 January 1977

Antarctic Marine Flora: Uniquely Devoid of Kelps

Abstract. *The discovery of embryonic stages of the common large Antarctic brown seaweed* Himantothallus *has led to the conclusion that this plant, hitherto assigned equivocally to the Laminariales (kelps), is a member of the Desmarestiales. Moreover, field study of a large sample of* Himantothallus *and two other enigmatic brown algae,* Phyllogigas *and* Phaeoglossum, *has led to the merger of these three genera with the recognition of a single species,* Himantothallus grandifolius. *The correct placement of these kelp-like algae underscores the uniqueness of the Antarctic marine flora as the only cold-water flora without kelps.*

In Antarctic waters, one of the largest, most abundant, and most widely distributed seaweeds is a kelp-like alga with a relatively short, often spirally twisted, flat stipe attached by a hapteroid holdfast and bearing one to several thick undivided blades up to 10 m long and 1 m broad. The earliest available epithet—*grandifolius*—is indeed appropriate. It was suggested by the Gepps (*1*), who first described this plant as a species of *Lessonia*, a widespread Southern Hemisphere kelp, based on material collected in 1902 by the British Antarctic Expedition. The correct generic name is equivocal. That it is clearly not *Lessonia* was recognized by Skottsberg (*2*), who proposed a new genus, *Phyllogigas*, to receive it. (*Lessonia* is characterized by progressive splitting of the thallus, beginning in the meristematic zone and proceeding toward the apex, a process lacking in the Antarctic plant.) In our opinion, three monotypic genera described from the Antarctic by Skottsberg (*2*), namely, *Phyllogigas*, *Himantothallus*, and *Phaeoglossum*, are growth forms of a single species, which for technical reasons given elsewhere (*3*) we have chosen to call *Himantothallus grandifolius*.

The taxonomic position of this extraordinary plant has been in doubt from the beginning. Two of its growth forms—*Phaeoglossum* and *Phyllogigas*—were assigned to the Laminariaceae by Skottsberg without reservation, although he was somewhat bothered by their vegetative structure, which suggested Fucales to him. A third growth form—*Himantothallus*—was placed by Skottsberg in the Fucales, but with much reservation. Zinova (*4*) proposed a new family, Himantothallaceae, which she considered to be intermediate between the Fucaceae and the Laminariaceae, and suggested the possible recognition of a new order, the Himantothallales. Skottsberg and Neushul (*5*) took cognizance of this idea, without committing themselves to further action. Reproductive structures, which were expected to help solve the problem, were not reported until 1963 (*6*). They turned out to be unlike those characteristic of either the Laminariales or the Fucales, but somewhat like those in the Desmarestiales.