Decomposition of Silver Acetylide

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Thermally unstable materials such as silver acetylide, which yield only solid decomposition products, differ significantly from materials having at least one gas among their products. Information about the mechanism of thermal and photodecomposition of silver acetylide is presented here. The decomposition of crystals of about 5 μ across produces carbon as an amorphous residue and silver of the hexagonal structure. The activation energy for thermal decomposition is 41 kcal/mole. The relationship between photodecomposition, absorption and photoconduction is investigated.

Recent studies of the properties of solid explosives have concentrated on those [1, 2] which yield a gaseous product.

The kinetics are in part controlled by the formation of surface vacancies as the gas evolves and by the mobility and nature of these vacancies, since the nuclei of the solid product appear to form within the holes formed by their aggregation.[3, 4]

Silver acetylide decomposes thermally according to

$$A(s) \rightarrow B(s) + C(s).$$

Since no vacancies arise from gas evolution, the kinetics are different and depend on whether both solid products are crystalline and require nucleus formation. Techniques designed to examine the formation and growth of nuclei, and to measure the related physical properties such as absorption, have been applied to silver acetylide to obtain more information about its decomposition mechanism.

EXPERIMENTAL

PREPARATION

Silver acetylide was prepared in two ways. By bubbling a stream of acetylene into an ammoniacal solution of silver perchlorate or silver nitrate, a precipitate of silver acetylide was obtained. After several washings with water containing acetylene, it was then placed on electron microscope grids while in suspension, or dried for use as a powder. Alternatively, when an atmosphere of acetylene is contained above the solution, a film which is useful for optical experiments forms at the interface. Because of the insolubility of silver acetylide, no method of preparing large single crystals was found.

The complex salt, $Ag_2C_2 . AgNO_3$, was also prepared as a powder and as a film, using an aqueous solution of silver nitrate of less than 10 % concentration. Concentrations greater than 25 % result in the production of a complex salt with a molar ratio of silver acetylide to silver nitrate of 1 : 6.[5, 6]

STRUCTURE OF MATERIALS

Sharp X-ray powder patterns of both compounds were obtained using an 18 cm Debye-Scherrer camera.[7] On the basis of these patterns, the crystal structure of silver acetylide is probably hexagonal with $a_0 = 6{\cdot}97_6$ Å and $c_0 = 12{\cdot}60_0$ Å.

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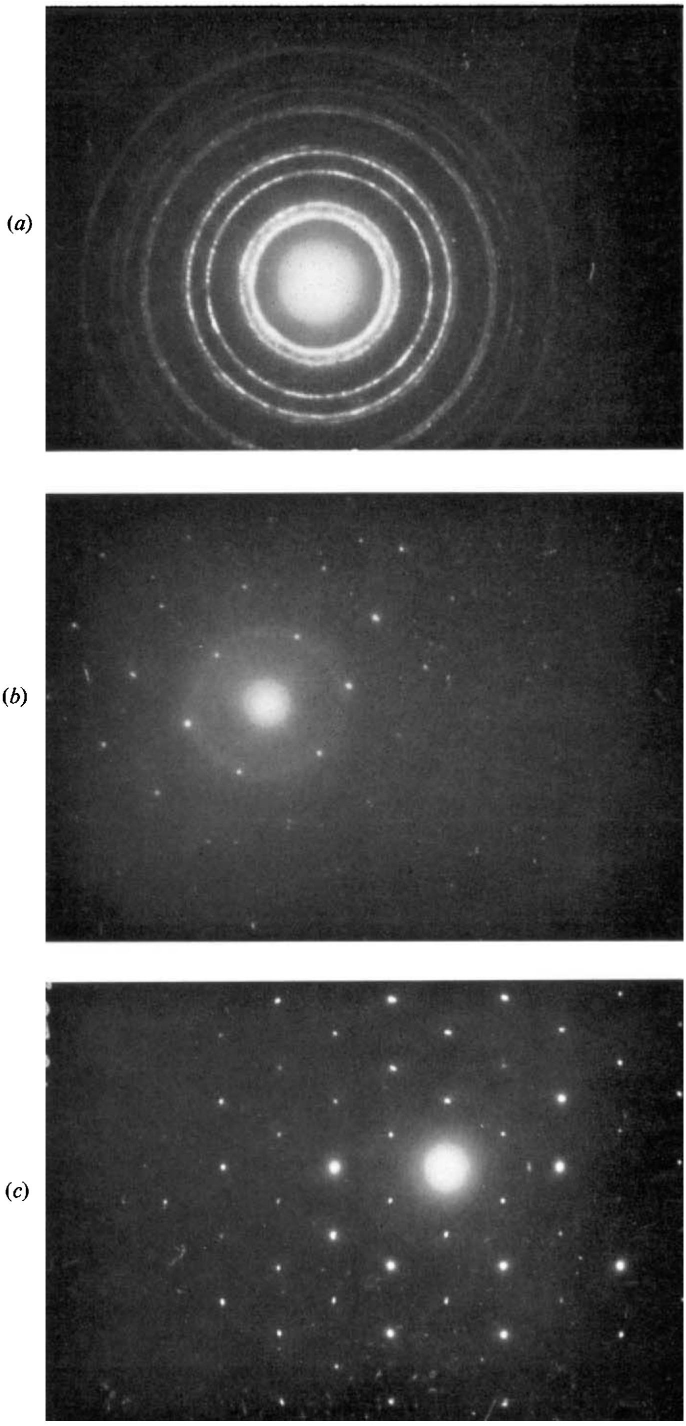

FIG. 1.—Electron diffraction patterns.

(*a*) Face-centred cubic silver; (*b*) single crystal of face-centred cubic silver; (*c*) single crystal of hexagonal silver.

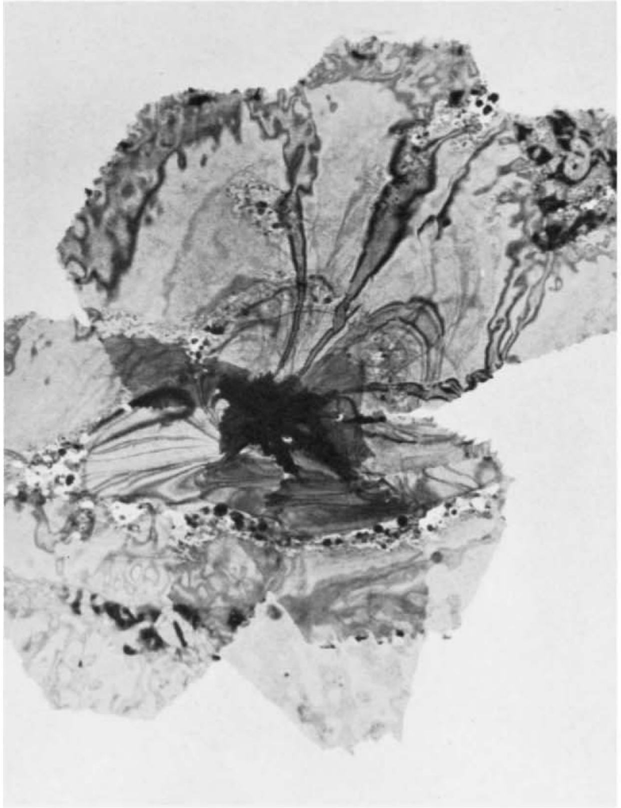

FIG. 2.—Silver of the hexagonal crystal structure.
Magnification is ×60,000.

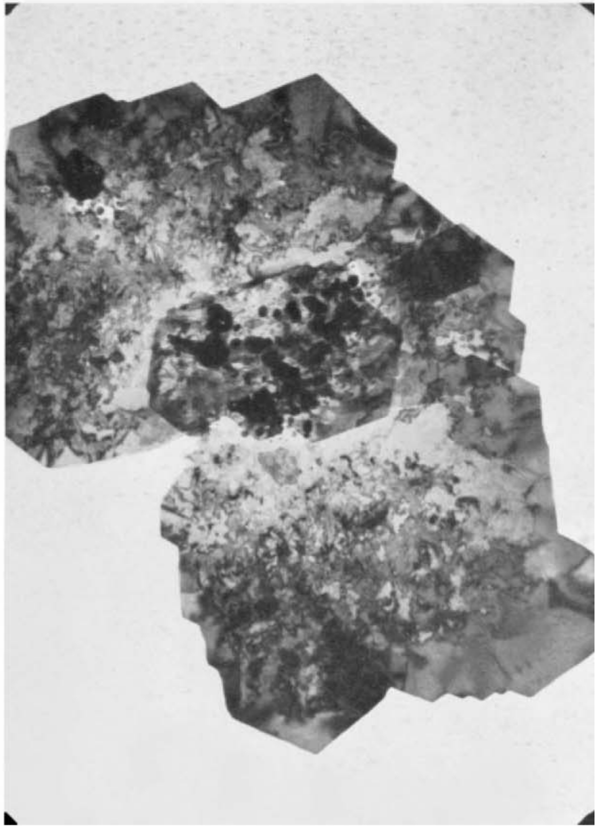

FIG. 3.—Silver of the hexagonal crystal structure.
Magnification is ×60,000.

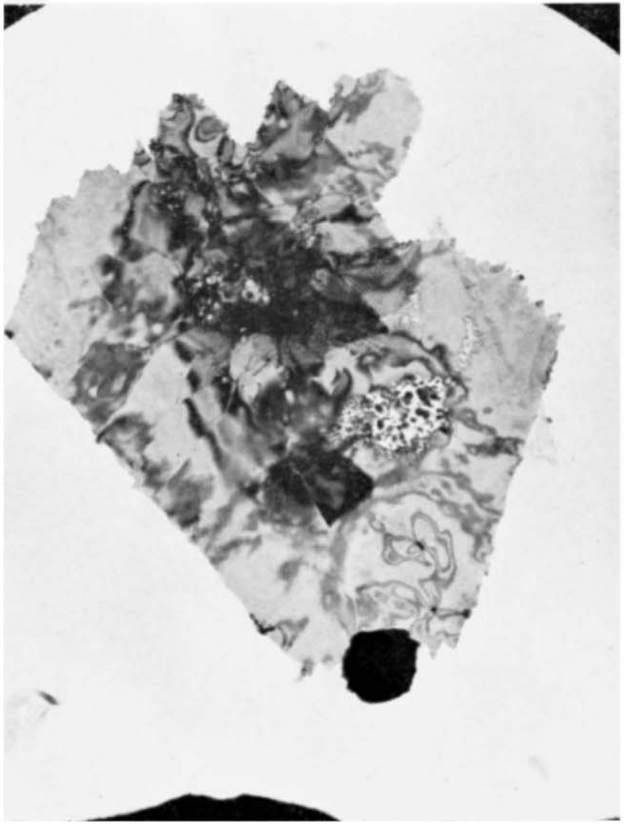

FIG. 4.—Silver of the hexagonal crystal structure.
Magnification is ×60,000.

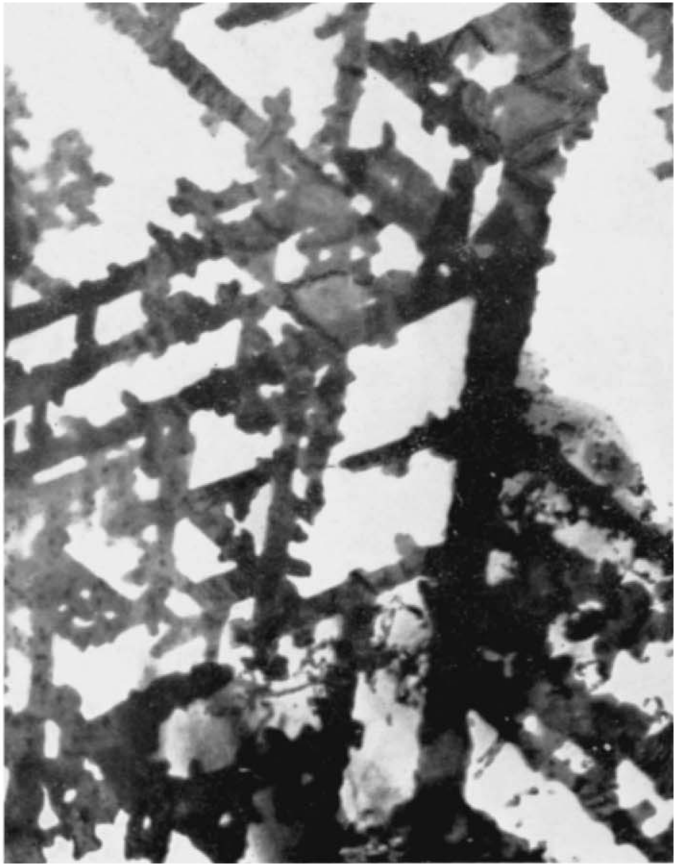

FIG. 5.—Silver of the hexagonal crystal structure.
Magnification is ×80,000.

Density measurements were made to check this structure, using a weighing bottle of less than 0·2 ml capacity. Both bromoform and water were used to measure the void space. Although the quantities were very small and the densities consequently somewhat imprecise,[7] the mean density of 4·47 g ml^{-1} agrees very well with the suggested structure and indicates that there are six molecules per unit cell.

Excellent powder patterns were easily obtainable from the complex salt but no structure consistent with these data could be found.[7]

THERMAL DECOMPOSITION

ELECTRON MICROSCOPY.—Both materials were examined using a Siemens Elmiskop 1 electron microscope. Grids of 500 bars/in. were used to improve cooling. However, both compounds proved to be too unstable in the electron beam for electron microscopy to be used to follow thermal decomposition, or to examine the growth of nuclei, even when cooled by liquid nitrogen.

When large quantities of material were decomposed, silver of the face-centred cubic structure and amorphous carbon were formed, usually adjacent to each other. Fig. 1*a* shows a typical diffraction pattern obtained from the silver.

When silver acetylide had been present as scattered crystals a few microns in diameter, decomposition was always complete before the sample was observable in the microscope. The silver produced was in the form of single crystals, almost always of the hexagonal structure. Typical crystals are shown in fig. 2 and 3, and a diffraction pattern is shown in fig. 1*c*. Rarely, discontinuities and Moiré patterns are observed as in fig. 4. A dendritic form of hexagonal silver, as in fig. 5, was also found a few times, diffraction patterns showing most " branches " to be part of a single crystal.

On a few occasions, single crystals of the face-centred cubic structure, oriented with the (110) planes orthogonal to the beam, have appeared. The diffraction pattern is shown in fig. 1*b*.

Amorphous carbon appeared as thick areas on the film often, but not always, adjacent to silver. Small opaque structures, such as those seen in fig. 2 and 3, commonly occur both near crystals of silver and in contact with them. These give no diffraction pattern but their frequency of occurrence on grids where no foreign material is observed indicates they may well be a carbon decomposition product.

The stability of the complex salt, $Ag_2C_2 . AgNO_3$, in the electron beam is not noticeably different from that of silver acetylide. The solid products are also similar, with face-centred cubic silver occurring if large masses are present, and hexagonal silver when only a little material is used. Some amorphous carbon is found.

For both compounds, the thermal decomposition products were examined using an X-ray powder camera. The only crystalline product was face-centred cubic silver.

ACTIVATION ENERGY FOR THERMAL DECOMPOSITION.—Silver acetylide, contained in a thin-walled quartz tube as used for X-ray powder photography, was decomposed thermally and the X-ray diffraction pattern obtained. Silver, of the face-centred cubic structure only, and amorphous carbon were the final products.

In order to obtain some measure of the activation energy of thermal decomposition, X-ray powder patterns were utilized to follow the decomposition of silver acetylide at 115°C, 125°C and 135°C. The dependence of the density of the lines of the powder pattern on the amounts of material present is complex and no effort was made to relate them directly. However, equivalent stages of decomposition at different temperatures can be determined at each point where the density of a silver line, increasing with each successive heating, becomes the same as that of a given silver acetylide line which decreases with each heating.

By measuring the density of certain lines from both the silver acetylide and silver from each pattern, and comparing the densities in this way, points of equal decomposition can be determined for different temperatures and the ratio of the times taken to reach each stage at two temperatures, the " time ratios ", noted. Densities were measured on a manual densitometer made by Hilger and Watt.

The method used was to heat the sample repeatedly, obtaining each time a powder pattern. A test was made to ensure that the result obtained by heating in stages for a given total time agreed with what would be obtained by heating it for the total period in one operation. The agreement was well within the error of this experiment.

Results indicate that the rate of thermal decomposition at 125°C is 4·1 times its value at 115°C and that the rate at 135°C is 3·3 times its value at 125°C. Assuming that the rate is $dx/dt = k(T)f(x)$, where x is the amount of silver acetylide present and that $k(T)$ has the form $k = A \exp(-E/RT)$, then E, a thermal activation energy, can be calculated from these data to be 41 ±4 kcal/mole.

PHOTODECOMPOSITION AND ABSORPTION SPECTRA.—The absorption of radiation of wavelengths from 2100 to 10,000 Å was measured for both silver acetylide and the complex salt, $Ag_2C_2 . AgNO_3$, using a Unicam spectrophotometer. Films of both materials of thickness ~0·1 mm were mounted on quartz discs 1·2 cm diam. The existence of tiny cracks, particularly in the film of the complex salt, made measurement of the absorption coefficients impossible. In fig. 6 and 7, silver acetylide exhibits a tailing off in transmission for wavelengths below 8000 Å and an abrupt fall below 3700 Å. The complex salt exhibits some tailing off, and a sharp fall at 3475 Å.

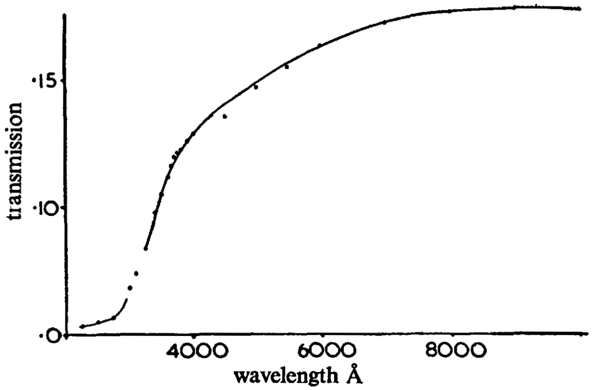

FIG. 6.—Absorption spectrum of silver acetylide at room temperature.

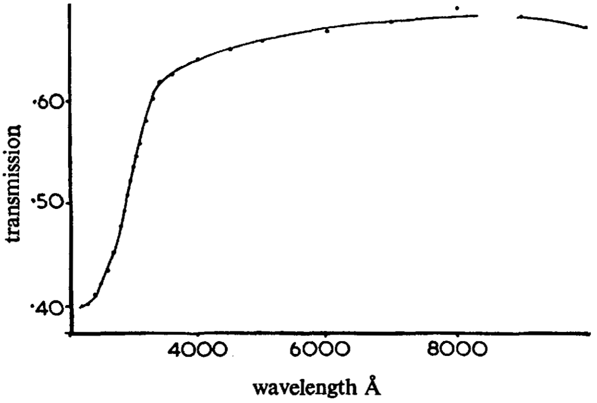

FIG. 7.—Absorption spectrum of the complex salt, $Ag_2C_2 . AgNO_3$, at room temperature.

Experiments, using the radiation from a mercury arc lamp and a series of filters, were performed to establish which regions of the spectrum were responsible for decomposition. It was shown that silver acetylide is decomposed very slowly by wavelengths above 5000 Å but more quickly as the wavelength was decreased; below 3500 Å, decomposition proceeded very quickly. For the complex salt, decomposition is rapid only for wavelengths below 3000 Å but some decomposition occurs, if slowly, up to at least 4500 Å. Irradiation darkens the surface of silver acetylide very quickly. However, the depth of this initial decomposition is slight. Very fine powder, when irradiated, turns black within a few minutes, but it can still be exploded after several days' exposure. Moreover, X-ray patterns obtained from such powder show no lines arising from silver, even after weeks of irradiation.

EXPLOSION

Silver acetylide was found to explode within 5-10 sec at temperatures between 195 and 200°C when small particles were dropped on to a clean mercury surface of known temperature. Results seemed independent of particle shape, and of size within the limits of 0·001-0·1 g; smaller particles sometimes failed to explode.

A Beckman and Whitley high-speed framing camera was used to measure the velocity of the movement of the front in explosion. Silver acetylide was packed in a trench 1 mm × 1 mm × 50 mm cut in a perspex plate, and ignited by an "exploding wire". A velocity of 1200 m/sec is reached within 1 μsec. Similar experiments with $Ag_2C_2 . AgNO_3$ showed an ignition temperature about 2°C higher than that of Ag_2C_2 and a detonation velocity of 1980 m/sec attained within 1 μsec.

DISCUSSION

Silver acetylide is a photoconductor at room temperature for all wavelengths from the ultra-violet up to at least 6000 Å.[8] Without measurements of both photoconductivity and absorption at low temperatures, however, it is not certain if the energy represented by the absorption edge at 3700 Å is sufficient to elevate an electron to the conduction band, or whether it produces an excited state from which thermal energy is capable of elevating the electron to the conduction band.

In the present work, photodecomposition occurs at the wavelengths at which the material is a photoconductor. McLaren and Rogers [9] suggest that with materials which are photoconductors under conditions where photodecomposition occurs, the rate-determining step is the production of free electrons. It is probable that the rate-determining step with silver acetylide is the production from the acetylide ion of an unstable carbon species and a free electron. This species will then decompose, producing amorphous carbon. The energy represented by the absorption edge is 3·34 eV or 76 kcal/mole. If this is the optical activation energy, the value is consistent with the thermal activation energy of 41 kcal/mole. Without values of the dielectric constants the activation energies can be compared only qualitatively.[10]

The mechanism suggested does not involve acetylide radicals combining. This is consistent with the finding of only amorphous carbon and is an important difference from materials such as the azides. It appears that, whereas both silver acetylide and silver azide exhibit photocurrent for wavelengths well outside the absorption edge, photodecomposition is much greater for silver acetylide in this region at room temperature. At such wavelengths, little absorption occurs and the population of excited levels is low. Thus, with the azide, the chance of two excited species being adjacent is small. With the acetylide, there is no such requirement and decomposition can occur whenever sufficient energy, optical and thermal, is supplied. Such a mechanism would also imply that the sensitiveness of the acetylides is less related to structure than is the case with the azides.[11]

The stable form for very thin silver crystals is the hexagonal form,[12] and the occurrence of this structure may arise simply from the crystals being thin. This is given support by the finding of hexagonal silver as a product of both compounds studied, although their own structures seem to be quite different. However, the appearance of the crystals, especially the formation of perfectly aligned "leaves" seen in fig. 2, may indicate growth from several nuclei whose structures are aligned by epitaxy.

The thermal decomposition of silver acetylide is catalyzed by the products,[11, 13] probably the silver nuclei. Explosion comes about through the accumulation of catalyst rather than of heat;[11] thus, the period before ignition is not closely correlated with particle size. It is noted that, although the products of decomposition are both solids at 200°C, detonation occurs. The period of low speed deflagration is very short.

It is not certain if migration over the carbon film is possible although silver is very mobile on other substrates. Carbon is often found remote from the silver crystals which suggests a migration of one or the other; it occurs too frequently to be entirely accounted for by the random deposition of silver and carbon produced by decomposition while in suspension. Moreover, hexagonal silver crystals were never found near large masses of silver of the face-centred cubic structure; this may indicate a high mobility permitting the migration of silver from small hexagonal crystals to a large mass of the face-centred cubic form.

The absorption spectra can be compared with the spectra of silver nitrate and the complex salt, $Ag_2C_2 . 6AgNO_3$.[8] The absorption edges occur at 3825 Å for silver nitrate, at 3750 Å for the 1 : 6 compound, at 3700 Å for silver acetylide and at 3475 Å for the 1 : 1 compound. This indicates that whereas in the 1 : 6 compound, relatively little distortion of the silver nitrate structure occurs, in the 1 : 1 compound a more ionic structure is produced, with a greater separation of the silver ions and anions.

The decomposition of the complex salt produces silver in both forms, as with the acetylide, and small amounts of amorphous carbon, as well as a variety of gaseous products, the small amount of carbon indicating the formation of one or both oxides of carbon.

It was shown earlier that the products of photodecomposition of silver acetylide form an opaque surface layer which prevents decomposition from proceeding, except extremely slowly, beyond a certain amount. Yoffe[8] has measured the photoconductivity of a pellet of silver acetylide before and after irradiation for 1 h with a mercury lamp, and found that the photocurrent was reduced at all wavelengths below 5800 Å after the irradiation and that it was almost eliminated at wavelengths below 3500 Å. This agrees with our results on the effect of different spectral regions on photodecomposition and the blockage of subsequent decomposition by the products on the surface. It implies that the wavelengths blocked by the surface layer are those which contribute most to decomposition, and that very long exposure will, eventually, decompose the material completely through the action of radiation of longer wavelengths.

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