Table 3. The flux listed in Table 3 applies to the two extended radio nebulas, exclusive of the central source. It was assumed that W_e is 1 percent of W_{CR}. The characteristic energy of relativistic electrons responsible for synchrotron radiation at 10^8 hz is given by

$$100 \text{ Mhz} = 4.2 \times 10^{-6} \gamma^2 H_\perp$$

where $H_\perp$ is in microgauss and γ, the ratio of relativistic electron energy to the electron rest mass, is given by

$$\gamma = \frac{E}{mc^2}$$

For $H_\perp = 4$ microgauss, $\gamma = 2.5 \times 10^3$ and $E \approx 10^9$ ev.

GEV electrons in a 2.7°K radiation field will produce x-rays by inverse Compton scattering in the energy range

$$E_{XR} \text{ (ev)} = 3.1 \times 10^{-4} \gamma^2 T \text{ (°K)} = 5000 \text{ ev}$$

which is the middle of the observed soft x-ray band (1 to 10 kev).

The power P of inverse Compton scattering per electron is

$$P = 2.7 \times 10^{-14} \gamma^2 \rho_{ph}$$

where ρ_{ph} is the energy density of photons whose wavelength is ~ 1 mm. For a radiation background temperature of 2.7°K,

$$\rho = 4 \times 10^{-13} \text{ erg/cm}^3$$

The total number of 10^9-ev electrons, on the basis of Ginzburg and Syrovatsky's value of

$$W_{CR} = 1.7 \times 10^{59}$$

and $k = 100$, is about 1.1×10^{60}. Accordingly, the total x-ray power, L_{XR} (Compton), should be 5×10^{40} erg/sec. This computed value is to be compared with the observed flux,

$$L_{XR} \text{ (obs)} = (1.1 \pm 0.4) \times 10^{41} \text{ erg/sec}$$

If the observed x-ray flux included an appreciable contribution from the central radio source, L_{XR} (extended source) should be somewhat lower for comparison with the theoretical Compton flux. In any case, the x-ray upper limit is consistent with a 3°K background. Shivanandan, Houck, and Harwit (*3*) have reported a flux of 5 $(+5, -2.5) \times 10^{-9}$ watt cm^{-2} steradian^{-1} in the band from 0.4 to 1.3 mm, which corresponds to $\rho_{ph} \approx 13$ ev/cm^3. For 2.7°K, the photon energy density is 0.25 ev/cm^3. The possible 50-fold infrared excess observed by the rocket instrument and a similar result recently obtained with a balloon-borne instrument (*4*) are inconsistent with the x-ray observation and the prediction of the radio model.

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18 June 1970

Induced Photolysis of DDT

Abstract. *Photolysis of mixtures of certain alkyl halides and aromatic amines produces dehalogenation of the halide. These reactions involve a photoinduced charge transfer from the amine to the halide. Photolysis of tritolylamine and carbon tetrachloride produces tritolylaminium chloride. Photolysis of 1,1,1-trichloro-2,2-bis(*p*-chlorophenyl)ethane (DDT) and diethylaniline at 3100 angstroms yields 1,1-dichloro-2,2-bis(*p*-chlorophenyl)ethylene (DDE), 1,1-dichloro-2,2-bis(*p*-chlorophenyl)ethane (DDD), *p,p′*-dichlorobenzophenone (DDCO), and hydrogen chloride. Photolysis of DDT does not occur unless an inducer which has a low ionization potential, such as diethylaniline, is present. The DDT-diethylaniline mixture is stable in the dark, and the induced photolysis is not affected by triplet quenchers.*

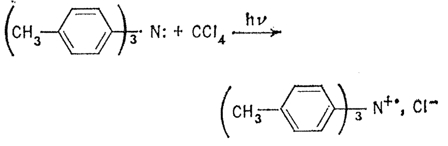
The pervasiveness of halogenated pesticides is a result of the resistance of these compounds and their progeny to environmental degradation. Utilization of solar energy is one approach to the decomposition of these compounds and, indeed, the photolysis of DDT (*1*) and of a number of other pesticides (*2*) has been studied. It is unfortunate that chlorinated hydrocarbons do not have a higher extinction coefficient ε in the solar region since this would undoubtedly lead to environmental photodegradation. An alternative approach is to induce their decomposition with other compounds which do absorb in the solar region. We report here on such a process and its application to DDT. This information may be useful for designing insecticides and understanding the environmental chemistry of such compounds.

This process involves the use of a sensitizer which is first photoexcited and then transfers an electron to organic halides. This should produce dissociation of the organic halide in analogy with a large number of chemical reactions of the type (*3*)

$$A \xrightarrow{h\nu} A^*$$

$$A^* + RCl \longrightarrow A^{+\cdot} + R\cdot + Cl^-$$

The photo-ionization of aromatic amines is a related process. Kadogen and Albrecht have, for example, studied the ionization of tetramethyl phenylenediamine in some detail (*4*). Hammill and co-workers (*5*) have recorded numerous examples of this phenomenon in glasses. They have also used alkyl halides to scavenge the dissociated electrons. Two closely related photoreactions have been studied in solution. While this study was in progress Tosa *et al.* (*6*) reported that dimethylaniline photolyzed in the presence of chlorobenzene produced benzene, biphenyl, and *N*-methylaniline. An excited charge-transfer complex was proposed as the critical intermediate. The photoinitiated reaction between carbon tetrachloride and primary aliphatic amines has received considerable attention (*7*). It has been proposed that in this case photolysis of a ground-state charge-transfer complex initiates a radical chain reaction. In each of these studies high concentrations were used. We here report the study of the photolysis of a number of aromatic amines and alkyl halides in dilute solution. Tritolylamine (386 mg) and carbon tetrachloride (1 ml) in 50 ml of acetonitrile, for example, were photolyzed in a Pyrex flask. A Rayonet reactor with 16 21-watt mercury lamps with major output at 3100 Å was employed. Within a few minutes the solution was deep green from an absorption band which developed at 6750 Å; maximum absorption occurred after 1.5 hours. This absorption band is characteristic of the tritolylaminium ion



which was independently prepared. Tritolylamine is not photooxidized in the absence of alkyl halide, and the mixture is stable in the dark. Similar results are obtained in the photolysis of triphenylamine and benzyl chloride or *tert*-butyl chloride or carbon tetrachloride. In these cases the triphenylaminium ion is not stable but forms the tetraphenylbenzidine cation radical and dication (*8*).

Table 1. Efficiency of induced photolysis of DDT.*

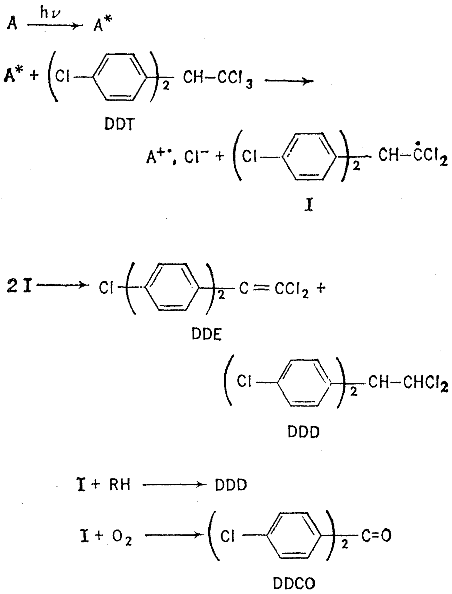
Inducer ($M \times 10^{-3}$)	HCl formed (moles $\times 10^5$)	DDT consumed (moles $\times 10^5$)	$\epsilon_{3100} \times$ concentration
None	0	0	
Triphenylamine (7)	1.3	6.5	120
Triphenylamine (7)†		6.5	
N,N-Diethylaniline (13)	16	8.7	23
N,N-Diethylaniline (13)‡		8.7	
N,N-Diethylaniline (13)§		8.7	
N,N-Diethylaniline (33) ||	57		
Benzophenone (6)	0	0	0.6
Quinoline (7)	0	0	18
Diphenyl sulfide (6)	1.5	2	0.6
p-Nitrotoluene (10)		0	2.8
p-Phenylenediamine (7)¶	20	6.5	3.3
1-Aminoanthraquinone (7)¶	0	0	35
Benzidine (6)¶	6.6	5.6	10

* Determined by irradiation of 100 mg of 98 percent *p,p′*-DDT in 50 ml of cyclohexane for 5 hours. † Solution was also 0.06*M* in naphthalene. ‡ Solution was also 0.2*M* in piperylene. § Solution was also 0.05*M* in naphthalene. || Irradiated for 15 hours. ¶ Solvent: 25 ml of cyclohexane plus 25 ml of isopropyl ether for solubility.

We studied the induced photolysis of 98 percent *p,p′*-DDT by photolyzing 50 ml of a solution of spectral grade cyclohexane, $2.82 \times 10^{-4}M$ in DDT and $\sim 10^{-2}M$ in inducer at 3100 Å (Table 1). A crude estimate of the extent of dechlorination was obtained by extracting the product mixture with water and titrating the acid in the aqueous phase. Similar results could be obtained if nitrogen is used to continuously sweep out the hydrogen chloride from the solution into the aqueous base. The analysis for DDT was performed by concentrating the extracted cyclohexane solution and submitting the mixture to gas-liquid chromatography. The glass column employed was packed with 10 percent silicone DC 200 plus 15 percent QF-1 on Chromosorb W. Quantitative comparisons should be made with caution since the organic products are a function of the inducer used and it is not known if all the light is being absorbed. It is clear, however, that compounds with a low oxidation potential are effective inducers. In contrast, benzophenone, aminoanthraquinone, and nitrotoluene are not effective and are difficultly ionized.

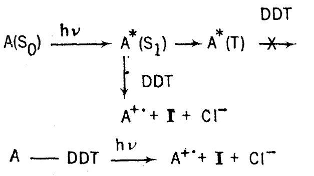
These results point to an electron-transfer process and seem to rule out an inducing mechanism involving energy transfer from the triplet state of the inducer to the organic halide (*9*). Energy transfer is not functionality-dependent but depends on the triplet-state energy E_T of the sensitizer. In this case benzophenone ($E_T = 69$ kcal) is completely ineffective as a sensitizer and triphenylamine ($E_T = 70$ kcal) is effective. Quenching experiments (see below) further rule out a triplet-state energy-transfer mechanism. We will, therefore, speak of inducers rather than sensitizers to differentiate between processes involving chemical reaction and those involving energy transfer.

The decomposition of DDT induced by the photolysis of diethylaniline produced DDD (6 percent), DDE (15 percent), and DDCO (16 percent). These were identified by comparing the retention times of the decomposition products in the gas-liquid chromatographic column with those of authentic samples and by mass spectroscopic analysis of fractions from a silica gel column. Two components of long retention time were also present. Triphenylamine induces the formation of DDD, DDE, and DDCO, and in this case the products of long retention time are not produced. The three products identified are very similar to products of the direct photolysis of DDT (*1*). It seems likely that they arise from a process involving radical **I**. The following is one mechanism consistent with the above results:



The decomposition proceeds at approximately the same rate in a closed flask or in a solution degassed by a nitrogen stream or by freeze-thawing. The formation of DDCO is, however, dependent on the presence of oxygen. The mechanism of DDCO production is not known, although several reasonable pathways which involve peroxy radicals can be imagined. The reactions of A+• depend on the structure of A. A blue-black polymer is, for example, formed from diethylaniline.

The nature of A* has been investigated by the addition of compounds that quench the triplet state. Photolysis induced by diethylaniline was not quenched by piperylene or naphthalene, and triphenylamine induction was not quenched by naphthalene. In each case, formation of a triplet excited state (A*) is feasible, but, since electron transfer from the triplet state of an amine would be an intermolecular process and cannot be quenched, this process is ruled out. Electron transfer from a singlet state of the amine (*6, 10*) and photolysis of a ground-state charge-transfer complex



remain mechanistically viable, as does a radical chain process.

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Phototropism in Phycomyces as Investigated by Focused Laser Radiation

Abstract. *The phototropic response and distribution of photopigment in the sporangiophore of* Phycomyces *was investigated with a microillumination pattern. The data support the hypothesis that phototropism results from greater stimulation of growth in regions of more intense illumination and indicate that the photoreceptor extends to the outer wall of the sporangiophore.*

The single-celled sporangiophore of the fungus *Phycomyces blakesleeanus* shows a positive tropic response to visible light (*1*, *2*). The focusing properties of the transparent cylindrical sporangiophore suggest that phototropism may be caused by increased growth in the region of most intense illumination (*2–4*); but no direct proof of this hypothesis exists. In addition, the location of the photoreceptor is unknown.

We report here the use of a microillumination pattern as a stimulus of the phototropic response in order to test the above hypothesis and to study the distribution of photopigment. A 488-nm laser beam was imaged through the sporangiophore in the shape of a thin plane parallel to the long axis of the sporangiophore (Fig. 1). The distance, *f*, of the plane of illumination from the axis could be varied. The components of the tropic responses in both the xz and yz planes were measured after a stimulus of 1 minute of laser illumination. The response in the xz plane (Fig. 2) began at 3 to 4 minutes and continued until 13 minutes. The tropic angle, ϕ, was taken as the change in inclination of the sporangiophore in the xz plane between 2 and 12 minutes as measured on the edge of the photograph nearest to the sporangium. The bend is clearly away from the side illuminated (Figs. 2 and 3A); the magnitude of the response depends on *f* (Fig. 3B). There was also a smaller but appreciable component of the tropic response in the yz plane. However, there was considerable scatter in these data and no apparent correlation in the sign or magnitude of the response with the position of illumination, which indicated that the tropism in the yz plane was random. Thus, the principal phototropic response is in the plane perpendicular to the direction of incidence. The receptor mechanism cannot sense the direction of incidence but responds to the differential illumination. Our results support the hypothesis that phototropism is caused by enhanced growth in the more intensely illuminated regions.

The appreciable tropic response stimulated by illumination near the outer wall indicates that some photoreceptor must extend to this region of the sporangiophore. To evaluate more specific distributions of photopigment, we constructed a simple model of the photoresponse. We assumed that any pigment in the light path is stimulated to produce a "growth factor" which diffuses randomly (in two dimensions for simplicity of calculation) until it reaches the outer wall (*5*). The inner membrane was treated as an impermeable reflecting boundary. The growth of each wall segment was assumed to be proportional to the amount of "growth factor" reaching that point and may be calculated by computer. The wall is elastic (*6*) and will bend to balance the internal forces set up by the uneven growth. The tropic angle was determined by a least-squares fit with the growth distribution.

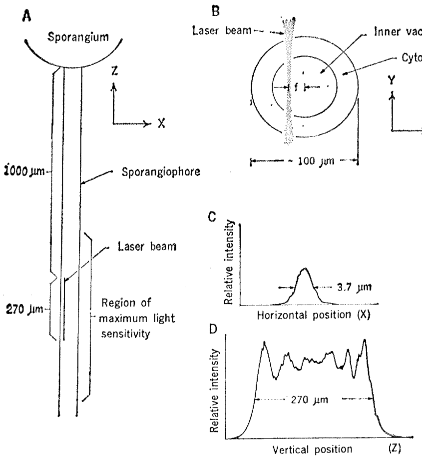

Fig. 1. (A) Schematic diagram of the sporangiophore and sporangium indicating the laser image as viewed along the direction of incidence. (B) Cross section of the sporangiophore. The path of the laser beam is shown assuming no scattering. Measurements of light scattering within the sporangiophore would better define the light distribution. (C) An experimental trace of the laser-beam intensity measured at the beam waist in the x direction. (D) An experimental trace of the laser beam intensity as measured along the sporangiophore axis (z).

Three hypothetical photoreceptor distributions were considered (Fig. 3B). The predicted tropic response for the pigment localized near the inner membrane is most clearly in disagreement with experiment. The assumption of a receptor near the outer wall also yields a large discrepancy between experiment and theory. Assignment of the photopigment to the cytoplasm or to both the inner and outer walls (curve not shown) gives predicted plots of tropic response which more closely correspond to our observations. The results indicate that the pigment cannot be confined to the region of the inner membrane and is probably not confined to the outer wall.

The laser, employed because of the collimation property of its radiation, was a continuous-wave argon laser at 488 nm operated in its lowest order spatial mode (T_{00q}) (*7*). The light, travelling in the y direction, was focused in the x direction by a cylindrical lens (2.5-cm focal length) forming a vertical line which was limited to 270 μm in length (along z) by a slit (Fig. 1, A and B). The width of the beam at the focus (Fig. 1C) was caused by diffraction associated with the 2-mm diameter of the beam at the lens. This configuration (f/12.5) was optimum for providing a narrow beam at the focus while avoiding large variations in beam width caused by focusing as the light traversed the 100 μm thickness of the sample. To obtain a nearly rectangular distribution of intensity in the z direction, Fresnel diffraction was minimized by placing the slits as close to the sample as was practical (*8*).

An inverted sporangiophore (Stage IVb) growing at a rate of 41 ± 9 μm/min in a shell vial of potato agar was held in a micromanipulator (*9*). The sporangiophore was immersed in a