importance but, as the trend toward diversification continues, may become more significant. The species of plants used in these experiments were:

Solanum tuberosum var. Chippewa
Lycopersicon esculentum var. John Baer
L. esculentum var. Southland
Solanum melongena var. Black Beauty
Capsicum annuum var. Calwonder
Brassica oleracea var. Golden Acres
Cucumis sativus var. David Bland
Allium cepa var. Yellow Globe
Zea mays saccharata

These plants were inoculated either by dipping the root system of the young seedlings in a heavy suspension of spores, sclerotia, and mycelia of *V. albo-atrum* and transplanting, or by working pure cultures of this fungus into the soil around the base of the plants. Control plants were maintained, and all the plants were allowed to grow for a period of 45 days. At the end of this period, attempts were made to recover the causal agent from all the plants inoculated.

V. albo-atrum B11B was recovered from two species of plants inoculated—namely, from the roots and aerial stems of 6 of 20 plants of *Solanum melongena* var. Black Beauty—and also from 4 of 20 plants of *Capsicum annuum* var. Calwonder, but only from the primary and lateral roots and never from the aerial stem.

These results seem to indicate that the isolate of *V. albo-atrum* from *M. piperita* is not as specific to that genus as has been believed.

The ability of *V. albo-atrum* B11B to exist as a saprophyte was determined by inoculating sterilized plant debris with pure cultures of the fungus. At the end of an incubation period of 30 days the relative amount of mycelial development was used as the criterion of the suitability of each substrate as a growth medium. The results of this experiment are shown in Table 1. It is to be noted that growth was excellent on *M. piperita* and *Chenopodium album*, and good on all other species except *Cannabis sativa*.

TABLE 1

Plant debris	Amt. growth
Solanum tuberosum L.	**
Lycopersicon esculentum Mill.	**
Capsicum annuum L.	**
Brassica oleracea L.	**
Mentha piperita L.	***
Amaranthus retroflexis L.	**
Chenopodium album L.	***
Portulaca oleracea L.	**
Cannabis sativa L.	*
Oenothera biennis L.	**

*** Excellent.
** Good.
* Poor.

The fact that the debris of *M. piperita* proved to be an excellent substrate is highly significant from the standpoint of control. After the oil has been distilled from the leaves and stems, the debris is used by many growers as organic fertilizer, and doubtless serves as a medium for propagating the fungus in the soil.

The final phase of this investigation dealt with the susceptibility of *M. piperita* to isolates of *V. albo-atrum* from other plants. Healthy plants of *M. piperita* were inoculated (via the soil, as in the previous experiments) with pure cultures of *V. albo-atrum* from potato, tomato, eggplant, nightshade, okra, honeydew melon, radish, boysenberry, and *Aralia japonica*. The results of these tests were negative except in two cases. *V. albo-atrum* No. 119 from tomato proved to be cross-infective with *M. piperita*, as did the isolate No. 53 from radish. In the latter case, however, the fungus was recovered only from the stem below the soil level and the smaller lateral roots of *M. piperita*.

From the standpoint of establishing a feasible crop rotation program to control peppermint wilt, our results seem to indicate that the natural flora and other economic plants of the muck soil regions of northern Indiana are relatively insignificant as hosts of *V. albo-atrum* B11B. Furthermore, our results show that this isolate is an efficient saprophyte and, barring inhibition by other microorganisms and environmental factors, it may persist on plant debris and in the soil for long periods of time. In addition, the results obtained indicate that *V. albo-atrum* B11B is not as specific in host range as previously believed. These results also support evidence from other sources for the existence of strains of *V. albo-atrum* which vary in host specificity and pathogenicity. Research now in progress is being done in an attempt to determine the stability of the proposed strains of the fungus *V. albo-atrum*.

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Formation of Thianthrene by a Free Radical Mechanism

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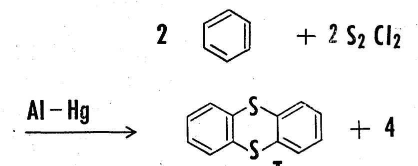
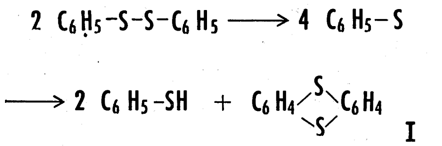
Cohen and Skirrow (*1*) observed the formation of thianthrene (I) from benzene and sulfur monochloride



I

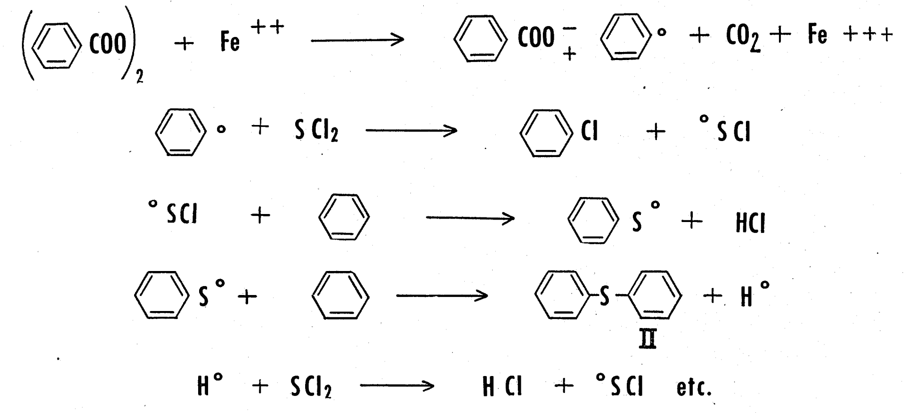
in the presence of an aluminum amalgam. These authors found that the reaction was very rapid and that the aluminum-mercury couple, used in small amount, was not affected by the reactants. These data seemed to indicate that the thianthrene was formed in this reaction via a free radical chain mechanism initiated by the aluminum-mercury couple. Schonberg (*2*) has observed the formation of thianthrene as a product from the dissociation of diphenyl disulfide into free radicals as shown in the accompanying equations.



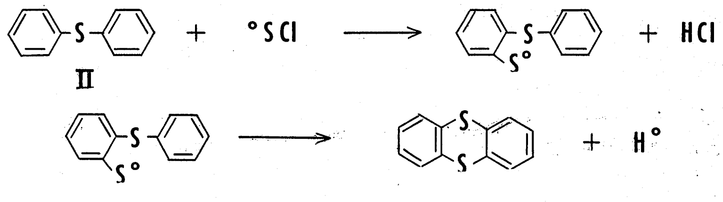
$$2\ C_6H_5{-}S{-}S{-}C_6H_5 \longrightarrow 4\ C_6H_5{-}S \longrightarrow 2\ C_6H_5{-}SH + C_6H_4\overset{S}{\underset{S}{\diagup\!\diagdown}}C_6H_4$$

I

We have found that thianthrene is formed in low yield by the reaction of benzene and sulfur dichloride (SCl_2) in the presence of benzoyl peroxide and a ferrous ion activation system (*3*). The thianthrene was not formed from benzene, sulfur dichloride, and ferrous salt under corresponding conditions of temperature and concentration, indicating that the presence of the peroxide was necessary for thianthrene formation. These data lead us to postulate that the thianthrene was formed as a result of the introduction into the system of free phenyl radicals from the benzoyl peroxide and the subsequent transformations represented below.



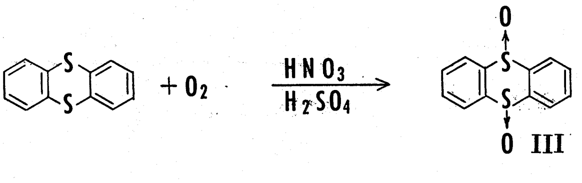
Thianthrene would result from an attack of another · SCl radical on the diphenyl sulfide (II) at the *ortho* position, followed by ring closure. There is the possibility here also for the formation of higher molecular weight polymer types by the attack of ·SCl at the *para* positions in diphenyl sulfide or at any position in a previously formed thianthrene molecule. We have some indications that considerable quantities of such polymers are formed.



The decomposition of SCl_2 by the phenyl radical, as represented in the second equation in the above series, is analogous to a reaction postulated by Kharasch and Brown (*4*) as an intermediate in the peroxide catalyzed chlorination of hydrocarbons with sulfuryl chloride.

$$R^{\cdot}\ (\text{from peroxide}) + SO_2Cl_2 \longrightarrow RCl + {}^{\cdot}SO_2Cl$$

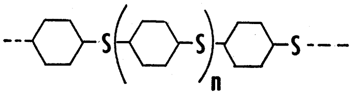
A mixture of 90 g (1.14 moles) of benzene, 60 g (0.57 mole) of sulfur dichloride, 2.4 g (0.02 mole) of ferrous carbonate, and 4.8 g (0.02 mole) of benzoyl peroxide was heated to reflux. There was a vigorous evolution of hydrogen chloride, which gradually subsided. After 6 hr of reflux, the mixture was distilled. After removal of volatile excess reactants, the residue was heated to 300° C under 30-mm pressure, and all distillate was collected. The small amount of distillate was washed with aqueous sodium hydroxide to remove benzoic acid. Thianthrene was difficult to isolate from the mixture directly, so it was oxidized under conditions found effective for converting thianthrene to thianthrene-5,10-dioxide (III), and the higher-melting, less soluble oxidation product was obtained and characterized as indicated in equation (III) above.



III

The residue from the sodium hydroxide wash above was suspended in 100 ml of concentrated sulfuric acid, cooled to the range of – 5 to 0° C, and 100 ml of fuming nitric acid (sp gr, 1.5) added over a 1-hr period, with stirring and cooling to maintain the temperature of the reaction mixture in the −5 to 0° C range. The mixture was allowed to stand for 1 hr at the same temperature, and the resulting clear solution was poured over crushed ice. The precipitated solid was removed by filtration, washed with water, and recrystallized from ethanol to yield 0.7 g (1.1%) of thianthrene-5,10-dioxide melting at 284–86° C. The literature reports the mp of this compound at 283–84° C (*5*). The 284–86° C melting product above was identical in mp and mixed mp with a sample prepared by oxidation in 80% yield of an authentic specimen of thianthrene by the same procedure used above. The thianthrene-5,10-dioxide was further characterized by its reduction with zinc dust and acetic acid to thianthrene according to the procedure of Krafft and Lyons (*5*). The thianthrene so produced was identical in mp and mixed mp with an authentic specimen.

A large amount of dark solid remaining in the reaction vessel after the distillation described above was ground to a fine powder and extracted repeatedly with carbon disulfide in order to remove occluded sulfur. The remaining solid was insoluble in all common solvents and melted above 300° C. This material was organic and possessed the properties of a polymer. A Parr bomb sulfur analysis on this product showed 35.95%. A polymer of the structure shown below would contain about 29.7% sulfur, as would other possible structures. The extra sulfur may be held in



$\overset{S}{\overset{\uparrow}{—S—}}$ type linkages or occluded mechanically. This product was formed in approximately 85% yield based on the assumption that it corresponded to the polymeric structure represented above.

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Acidimetric Titration of Alkali Chloride and Hydrochloride Salts

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Although chlorides, such as sodium and potassium chloride, are generally considered to be model examples of neutral salts, this is only relatively true. We have recently been able to titrate these, as well as hydrochlorides of amines, as bases with perchloric acid, using acetic acid as the solvent. In glacial acetic acid, which is considerably less protophilic than water, hydrochloric acid is largely unionized, being one of the relatively weaker inorganic acids, and is readily volatile. The titration of these salts in acetic acid would then be analogous in a sense to titration, for example, of alkali carbonates in water.

TABLE 1

TITRATION OF PROCAINE AND PROCAINE HYDROCHLORIDE IN GLACIAL ACETIC ACID

Sample	Equiv/mole found
Procaine	1.96
	1.96
	1.97
Procaine hydrochloride	1.92
	1.94
	1.94
	1.93
	1.95

Although acidimetric titration of bases in acetic acid with perchloric acid is a relatively well-established method (*1*), there appears to be no reference in the literature to the possibility of titrating chloride salts in this medium. We ourselves were led to this observation during a more or less routine application of the glacial acetic acid-perchloric acid method to the analysis of procaine and procaine hydrochloride. As expected, two equivalents of perchloric acid were required to neutralize the base. We were surprised to find, however, that the hydrochloride salt also required nearly two equivalents per mole. This seemed to indicate that hydrochloric acid was too weak an acid to affect the indicator, α-naphthobenzein, in the solvent employed. This conclusion pointed to the possibility of direct acidimetric determination of any chloride salt.

In order to test this possibility, the method has been applied to sodium, potassium, and ammonium chloride in addition to procaine hydrochloride.

The following procedure was employed in obtaining the data reported:

The weighed sample (0.1–0.5 g) was placed in a

TABLE 2

ACIDIMETRIC TITRATION OF SODIUM, POTASSIUM, AND AMMONIUM CHLORIDE

Sample	Equiv/mole found	Indicator
Sodium chloride	0.997	α-Naphtholbenzein
	1.001	
	0.994	
	0.996	
Potassium chloride	1.016	Methyl violet
	1.018	
	1.024	
	1.020	
	1.020	
Ammonium chloride	1.000	α-Naphtholbenzein
	1.002	
	0.995	
	0.994	
	1.005	