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VAPOR-PHASE PHOTODECOMPOSITION OF p,p'-DDT

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Return to WPR File DDT Photodecomposition to Chemistry

by

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INTRODUCTION

Recent work on global modeling of pesticides in the environment has confirmed the worldwide presence of DDT in the atmosphere (1-3). These air-borne residues result from the relatively high vapor pressure of DDT (4,5) which assures direct losses from plants and soil into the atmosphere, and from adsorption to dust particles, followed by transport to remote areas. The persistence of DDT often results in losses to the atmosphere rather than chemical degradation in plants and soil.

DDT residues in rainwater suggest a mean residence time for the compound in the atmosphere of approximately four years (6). Hence, there is sufficient time for global transport and photochemical degradation of DDT by the ultraviolet (UV) component of sunlight.

Since previous work on the photochemistry of DDT in condensed phases has revealed that photodegradation by sunlight takes place very slowly, it has been assumed, by some, that the vapor-phase photolysis would be negligible. In order to estimate whether atmospheric degradation of DDT by sunlight actually might be important, we conducted tests, under NSF sponsorship, in the vapor-phase photoreactor which we described last year at the 163rd national meeting of the American Chemical Society at Boston, Massachusetts.

Before discussing the vapor-phase photolysis of DDT, I would like to describe the reactor and the light source.

The first slide (Fig. 1) shows a photograph of the vapor-phase photoreactor. The large sphere is the reaction chamber while the UV lamp is housed in the light shield at the right. The cylinder at the left serves as a light trap and the heating mantle provides gentle heat to enhance volatilization of the pesticide which is contained in the bottom of the reaction chamber.

In order to describe the vapor-phase photoreactor in greater detail, a

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schematic drawing of it is shown in the next slide (Fig. 2). Photochemical studies of pesticides are conducted by delivering a collimated beam of UV light through the center of the reaction chamber which is saturated with pesticide vapor. After the light has passed through the reaction chamber it is absorbed by a light trap to prevent it from reflecting back onto the reactor wall.

The reaction chamber is a 72-liter pyrex round bottom flask which has a dull black finish on its outer surface. An uncoated circular area, 6 inches in diameter, is located opposite the collimator in order to permit the beam of light to leave the reaction chamber and be absorbed by the light trap. A 3 mm thick pyrex disk is bonded to one end of the collimator to prevent the escape of pesticide vapor and to filter the light entering the reaction chamber. Since pyrex glass only transmits wavelengths greater than 300 nm, the disk ensures that the light entering the reaction chamber is no more energetic than that which reaches the lower atmosphere of the earth.

The light trap has a dull black finish and is placed over the uncoated area, or "window," of the reaction chamber to absorb the collimated beam of light after it leaves the reactor.

In order to saturate the reactor with pesticide vapor, 5 mg of the chemical under investigation is coated on a watch glass which is then placed at the bottom of the reaction chamber. A heating mantle positioned directly beneath the reactor is used to apply gentle heat (ca 35°) to enhance volatilization of the pesticide.

Gas inlet and outlet tubes of 5 mm glass tubing provide vents to the outside or may be used to circulate air, or an inert gas, through the reaction chamber. These tubes could also be used to remove volatile photoproducts to an absorption train. In the experiments described in this paper, they were used as vents.

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As one can see from the schematic drawing, the area of the reactor wall that is exposed to light is at a minimum compared to the volume described by the beam of light. Hence, by using this type of reactor design, vapor-phase transformations are much more probable than wall reactions.

In order to detect wall reactions, the wall of the reaction chamber is intentionally irradiated with light. This is accomplished by replacing the light trap with a spherical mirror which is shown in the next slide (Fig. 3). The reflector is a silvered one-liter round bottom flask which was chosen because it has the ideal curvature for uniformly reflecting the collimated beam of light back onto the walls of the reactor. As the slide illustrates, light rays near the center of the collimated beam are reflected through small angles while those at the outer edge are reflected through larger angles. The uniform distribution of light at the "window" results in a uniform reflection of light back onto the reactor wall. Any photoproduct that results from a wall reaction should be produced in greater yield when the photolysis is conducted with the mirror rather than the light trap since much more light reaches the reactor wall when the mirror is used. Hence, wall reactions are detected by comparing the product distributions or gas chromatographic profiles from two photolyses, one employing the light trap and the other the mirror. If these profiles are essentially the same, the likelihood is that all of the transformations are taking place in the vapor-phase while any substantial differences would probably be due to wall effects.

The next slide (Fig. 4) shows the spectral energy distributions of a number of light sources. Band "A" is the 254 nm line from a low pressure mercury arc lamp. Curve "C" is the distribution for an F40BL lamp and curve "D" is the distribution for sunlight. A comparison of curves "C" and "D" shows that the F40BL provides an excellent simulation of sunlight between 290 and 330 nm.

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The heavy line represents the distribution for a GE "RS" sunlamp which was used for the photolysis of DDT. The bands that are cross hatched represent the distribution of the light source we used and reported last year, a mercury arc lamp. The sunlamp is a much better simulator of sunlight than the mercury arc because of its output between 290 and 360 nm. The broken curve "B" is the transmission line for pyrex glass. By using a GE "RS" sunlamp with a pyrex filter, one obtains an excellent simulation of sunlight between 290 and 310 nm which is a crucial region for pesticide photochemistry.

To study the vapor-phase photochemistry of a chemical, three reactors are used simultaneously. Photolyses are conducted in two of the reactors with all conditions identical except that one employs a light trap and the other a mirror. The third reactor serves as a dark control with all conditions identical to an actual photolysis except that light is not used. In each photolysis, 5 mg of the chemical is volatilized from the bottom of the reaction chamber at 35°C and irradiated for 4 days.

The analytical method consists of rinsing each reactor with 5,400 ml portions of hexane. The rinses are combined, concentrated to a small volume on a rotary evaporator and analyzed by combined gas chromatography-mass spectrometry. Hence, three samples result for each chemical studied and are referred to as the "trap," "mirror," and "dark control."

The next slide (Fig. 5) shows the GC profiles obtained from the vapor-phase photodecomposition of p,p'-DDT. The dark control indicates the absence of dark reactions and artifacts. The profiles from the light trap and mirror each reveal two photoproducts, p,p'-DDE and p,p'-DDD. The close similarity of the two profiles indicates that both of these transformations are taking place in the vapor-phase. Since the conversion of DDT to DDE involves the loss of a molecule of hydrogen chloride, this transformation could occur by way of a uni-

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molecular process where collision with another molecule is not required.

The conversion of DDT to DDD requires the presence of a hydrogen donor as this transformation involves the replacement of a chlorine atom by a hydrogen atom. There are two sources of hydrogen inside the 72-liter reaction chamber: water vapor and DDT and its breakdown products. While there is a large excess of water vapor present (ca ten thousand fold), water is not a good hydrogen donor. The low frequency of collisions between DDT molecules rules out DDT as the source of hydrogen. This conversion could be a wall reaction that is limited by lack of a good hydrogen donor. In this case, the trap and mirror samples would have small, but equal amounts of DDD since the limiting factor would not be the amount of light reaching the reactor wall, but the amount of hydrogen donor present in the reaction chamber.

The next slide (Fig. 6) contains the quantitative data for the vapor-phase photodecomposition of p,p'-DDT. As the GC profiles indicated, DDE is the major photoproduct and is produced in yields of 1.3 mg and 1.5 mg with the light trap and mirror respectively. The yield of the minor photoproduct, DDD, is the same for both the light trap and the mirror, 0.1 ng. Hence, the rate of conversion of DDT to DDE is approximately fifteen times as fast as that for DDT to DDD with 34 percent of the DDT being photolyzed in 4 days.

Irradiation of p,p'-DDD for a period of 4 days resulted in no photolysis and apparently represents an endpoint as far as the vapor-phase photodecomposition of DDT is concerned.

Irradiation of 5 mg of p,p'-DDE for a period of 4 days resulted in the formation of small amounts of a number of photoproducts which are listed in the next slide (Fig. 7). The dark control contained only DDE and a small amount of dichlorobenzophenone. The profiles from the trap and mirror were essentially identical with each containing 9 peaks.

The first peak had a parent ion at m/e 222 and contained 2 chlorine atoms. The mass spectrum and retention time of this compound were identical to those for a standard of 4,4'-dichlorobiphenyl. In the absence of other spectroscopic data, an exact structural assignment cannot be made, but it is most probably either 4,4'-dichlorobiphenyl or 3,3'-dichlorobiphenyl.

The second peak has a parent ion at m/e 236 which corresponds to the molecular formula $C_{12}H_6Cl_2O$ with fragments at P-35 and P-70. This mass spectrum suggests a fused or bridged aromatic ring system containing a phenol group.

The third peak has a parent ion at m/e 256 with three chlorine atoms and a mass spectrum which is qualitatively identical to that for a standard of 2,4,5-trichlorobiphenyl. The low yield of this product makes an exact structural assignment very difficult.

The fourth peak represents the major photoproduct, 4,4'-dichlorobenzophenone.

The fifth peak has a parent ion at m/e 282, but its spectrum and retention time are different from those for DDMU. Its molecular formula is $C_{14}H_9Cl_3$.

The sixth peak has a parent ion at m/e 290 and contains 4 chlorine atoms. Its mass spectrum is qualitatively identical to that for a standard of 2,5,2',5'-tetrachlorobiphenyl, but as in the case with the trichlorobiphenyl mentioned earlier, the paucity of material precludes an exact structural assignment.

The seventh peak represents the second most abundant photoproduct, DDMU. The formation of DDMU from DDE is analogous to the formation of DDD from DDT. A hydrogen abstraction is taking place which requires the presence of a hydrogen donor. Considering the small amount of this product formed relative to DDE, there is a strong possibility that DDMU arises by way of a wall reaction

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with the rate determining factor being the availability of a hydrogen donor.

The eighth peak has a mass spectrum which is very similar to DDE, but has a different retention time. The structure of this compound is not known, but has been referred to by some as the "DDE isomer." Currently, more of this compound is being generated in order to obtain an NMR spectrum which may permit an exact structural assignment to be made.

The ninth peak has a parent at m/e 250 and contains 2 chlorine atoms. While it has the same parent ion as dichlorobenzophenone, the rest of the spectrum is not the same. The fact that it is poorly resolved from the large excess of starting material makes structure elucidation difficult.

The tenth peak represents the large excess of starting material, DDE.

Since 4,4'-dichlorobenzophenone and DDMU were the major products from DDE, their photochemical behavior was investigated. When DDMU was irradiated, it was converted at a moderate rate to 4,4'-dichlorobenzophenone indicating that it is an intermediate in the photolysis of DDE.

Irradiation of 4,4'-dichlorobenzophenone resulted in the formation of a small amount of dichlorobiphenyl. The slow reaction rate for this conversion explains both the accumulation of dichlorobenzophenone and the formation of dichlorobiphenyl from the photolysis of DDE. Prolonged irradiation of 4,4'-dichlorobiphenyl did not result in any further photolysis which indicates that this compound represents an endpoint in the photolysis of DDE.

DISCUSSION

The next slide (Fig. 8) summarizes the overall vapor-phase photodecomposition of DDT. These rates indicate that when DDT vapor is exposed to sunlight it will be rapidly converted to DDE which will accumulate because its rate of photodecomposition is much lower. Hence, the ratio of DDE to DDT should in-

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crease with time in air samples containing DDT.

The much slower rate of conversion of DDT to DDD is probably due to a lack of a good hydrogen donor. Hence, the rate of formation of DDD from DDT in air samples will probably be very dependent on atmospheric conditions. DDD would be expected in areas where the atmosphere contains large amounts of particulate matter and good hydrogen donors such as hydrocarbons. Once formed, the DDD would be very resistant to further breakdown in the atmosphere.

Since the photodecomposition of DDE requires a good hydrogen donor and perhaps "surfaces," its fate also could be expected to be strongly influenced by local conditions with particulates and hydrocarbons causing it to disappear much faster.

The major photoproducts of DDE, 4,4'-dichlorobenzophenone and DDMU, are formed in high enough yields that they could be detected in air samples containing DDE. Since dichlorobiphenyl is formed from dichlorobenzophenone and is resistant to further breakdown, it would be expected to accumulate, but the probability of detecting it in air samples containing DDE is remote. However, its gradual formation in air combined with its detection in such places as oil slicks or suspended organic matter.

The trichlorobiphenyl and tetrachlorobiphenyl were formed in much lower yield than the dichlorobiphenyl, but again their resistance to further degradation may result in their accumulation and detection in organic matter.

Since the exposure of thin films of DDE to sunlight results in the formation of significant amounts of 3,6-dichlorofluorenone, which is a type of biphenyl, the question arose as to whether this compound may also be a precursor to the dichlorobiphenyl found in the photolysis of DDE. However, the 3,6-dichlorofluorenone proved to be resistant to further hydrolysis and did not produce any dichlorobiphenyl.

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The vapor-phase photolysis of DDT is in marked contrast to its photodecomposition in condensed phases in which DDT is slowly converted to DDE which is in turn rapidly broken down, with the end product being dichlorobenzophenone. This contrasting photochemical behavior of DDT may account for its environmental fate. Since DDT is resistant to breakdown in soil and water, most of it is lost to the atmosphere by evaporation, followed by its facile conversion to DDE. Upon returning to the earth, the DDE would be subject to rapid breakdown by light or metabolic processes. On the other hand, if the DDE remains airborne long enough, substantial amounts of it could be converted to the di-, tri- and tetrachlorobiphenyls, which being resistant to further degradation, would mean that one environmental contaminant has been replaced by another.

Further experiments in which particulate matter and hydrocarbons will be present during the photolysis may reveal to what extent the vapor-phase photolysis of DDT is influenced by atmospheric conditions.

If field studies confirm the photochemical behavior observed with our photoreactor, then laboratory studies with this apparatus will definitely indicate patterns of environmental attention.

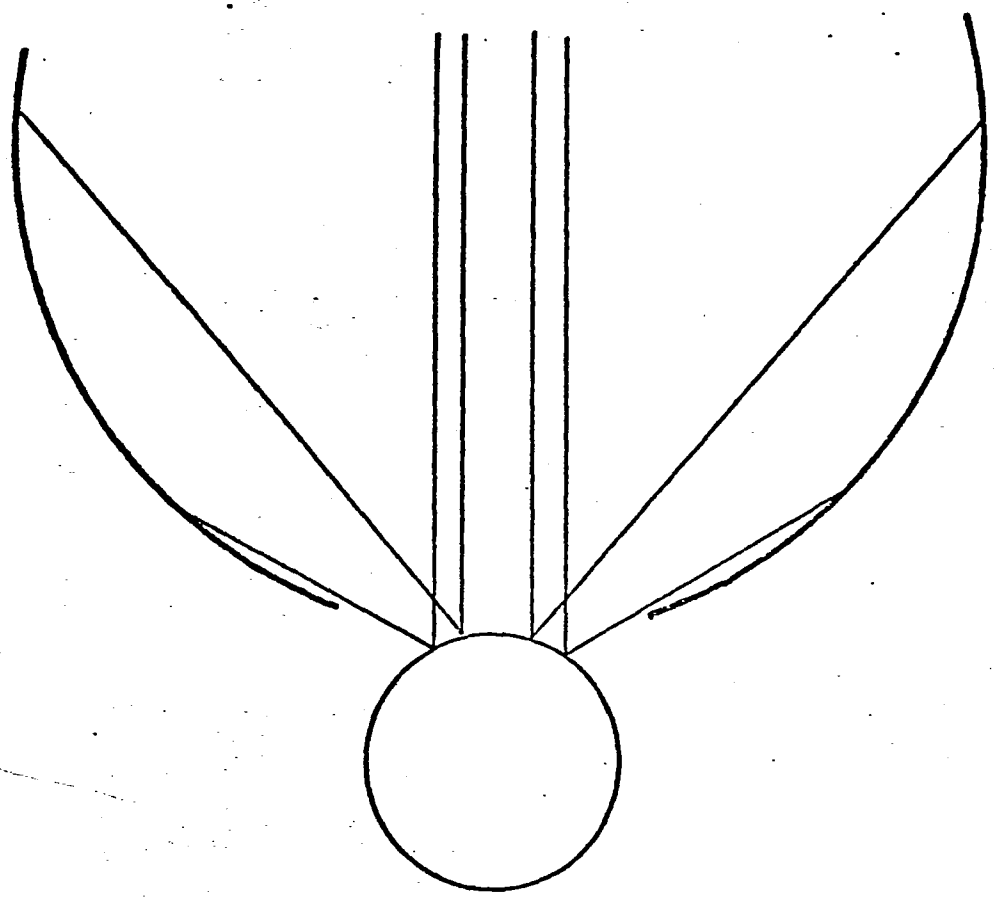
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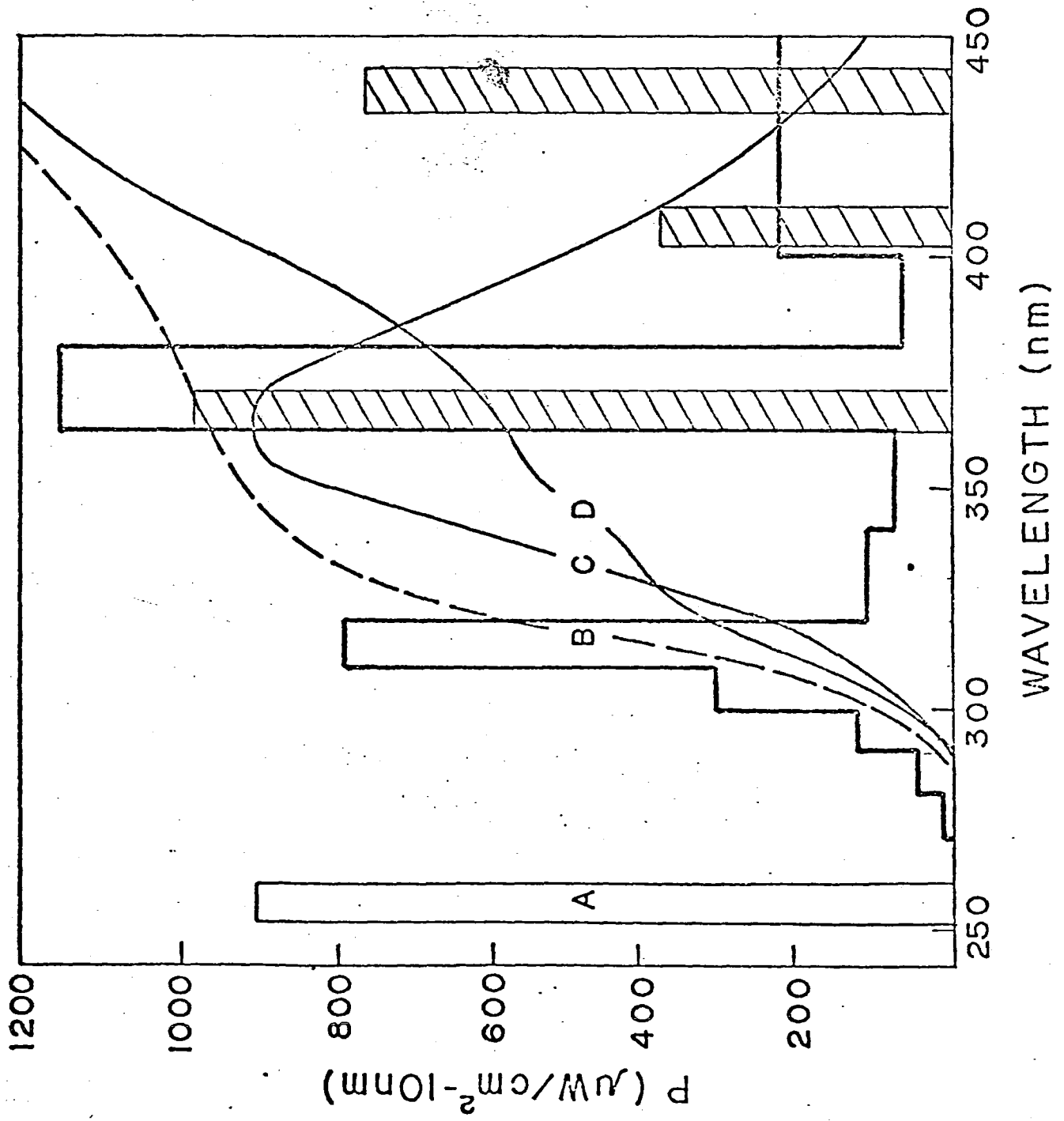
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UV LAMP
LIGHT SHIELD
AIR
COLLIMATOR
12-1/4"
31-1/4"
REACTION CHAMBER
HEATED DISH
LIGHT TRAP

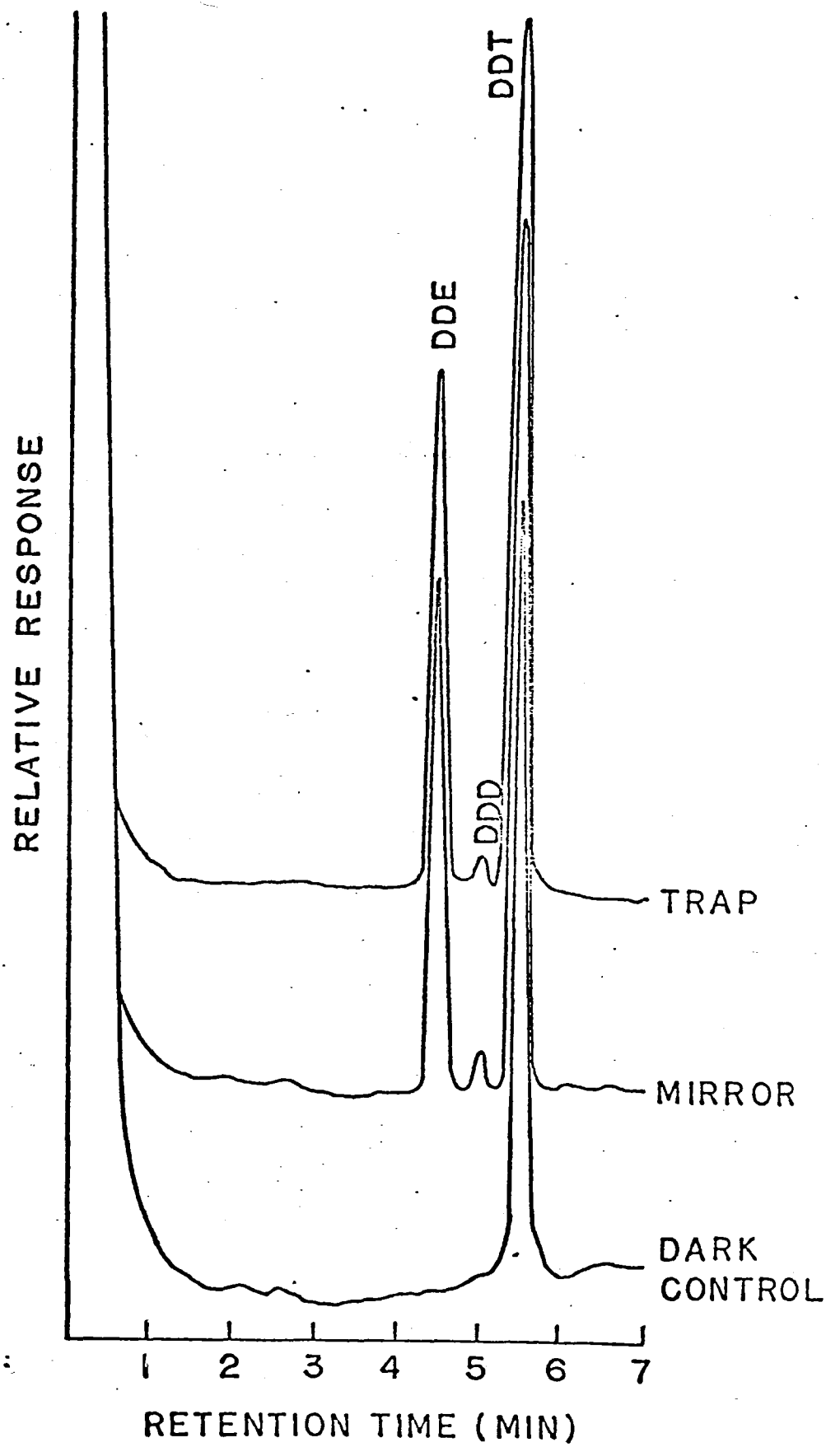
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DSW 346170


P (μW/cm²-10nm)
1200
1000
800
600
400
200
WAVELENGTH (nm)
450
400
350
300
250
A
B
C
D

DSW 346171



DSW 346172

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Vapor-Phase Photolysis of p,p'-DDT[a]

	p,p'-DDE	p,p'-DDD	p,p'-DDT
	mg	mg	mg
Light trap	1.3	0.1	3.4
Mirror	1.5	0.1	3.2
Dark control	<0.01	<0.01	5.0

[a]5 mg of p,p'-DDT was irradiated for 4 days

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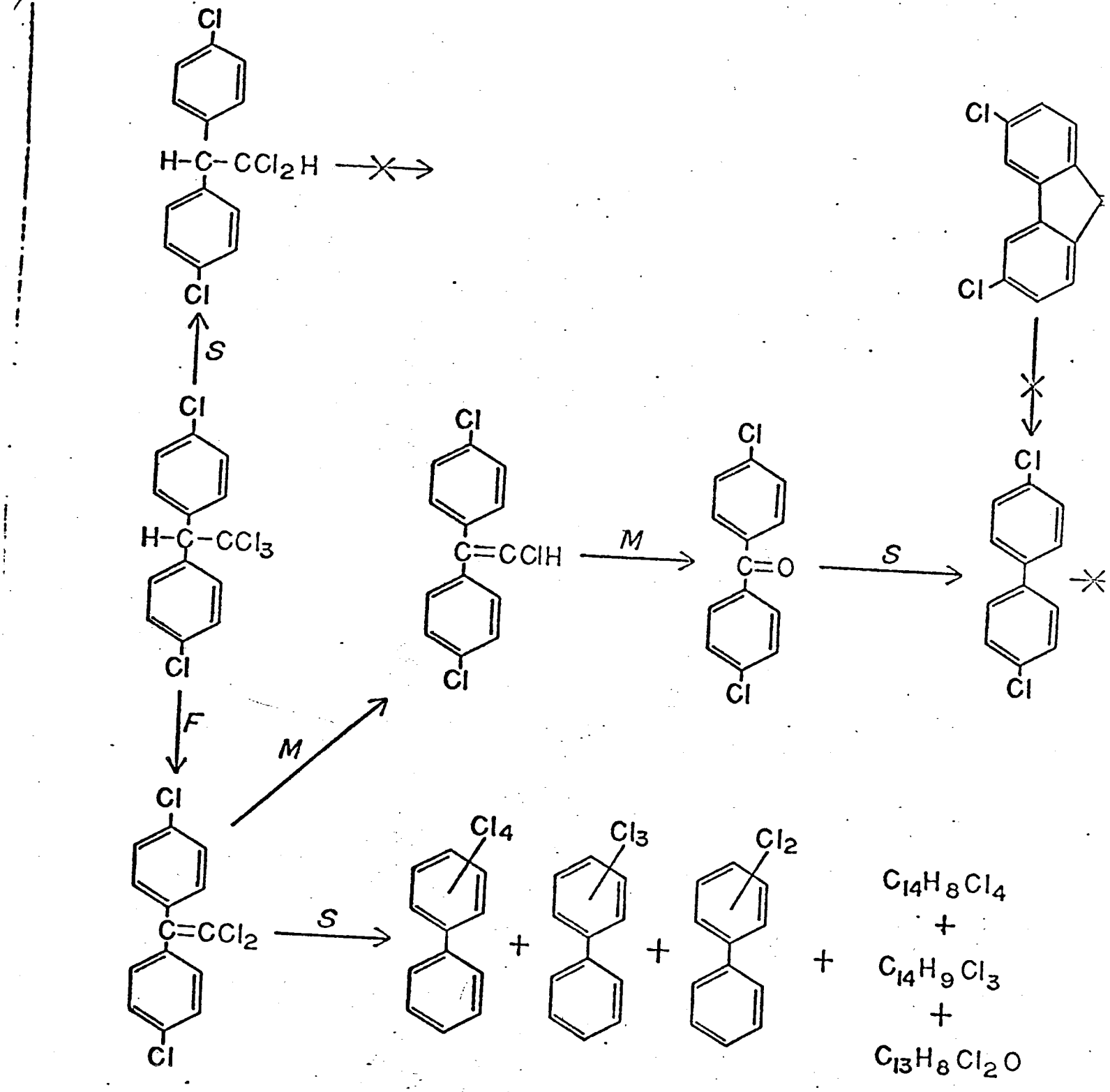
Vapor-Phase Photolysis of p,p'-DDE[a]

	Light Trap[b]	Dark Control
	µg	µg
Dichlorobiphenyl	20	<2
$C_{12}H_6Cl_2O$, m/e 236	2	"
Trichlorobiphenyl	2	"
4,4'-Dichlorobenzophenone	60	3
$C_{14}H_9Cl_3$, m/e 282	20	<2
Tetrachlorobiphenyl	5	"
DDMU	40	"
$C_{14}H_8Cl_4$, m/e 316	30	"
$C_{13}H_8Cl_2O$, m/e 250	20	"
p,p'-DDE	4800	5000

[a] 5 mg of p,p'-DDE was irradiated for 4 days

[b] Identical results were obtained with the mirror

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