

Vapor Pressures and Relative Volatility of Ethyl and Methyl Parathion

William F. Spencer,* Thomas D. Shoup, Mark M. Cliath, Walter J. Farmer, and Rizwanul Haque

Vapor pressures of ethyl parathion (*O,O*-diethyl *O*-(*p*-nitrophenyl)phosphorothioate) and methyl parathion (*O,O*-dimethyl *O*-(*p*-nitrophenyl)phosphorothioate) were measured using a gas saturation technique and polyurethane foam vapor traps. The vapor pressure, in mmHg, of ethyl parathion was linearly related to reciprocal temperature by the equation $\log P = 12.66 - (5274/T)$. With methyl parathion, apparently heat of vaporization changes at the melting point of 35.2–35.4 °C and the equations $\log P = 14.37 - (5700/T)$ and $\log P = 10.61 - (4543/T)$ describe the vapor pressure–temperature relationship below and above the melting point, respectively. The vapor flux of ethyl and methyl parathion at 25 °C from nonadsorbing surfaces was 0.210 and 0.435 $\mu\text{g} (\text{cm}^2)^{-1} \text{h}^{-1}$, respectively, which is directly proportional to their relative vapor pressures. Vapor loss rates from soil-incorporated methyl parathion were much lower than those from glass surfaces.

Reliable vapor pressure values of pesticides at various temperatures are basic to predicting their vaporization rates. A search of available literature on the vapor pressure of 49 commonly used pesticides showed different authors reported widely variable vapor pressure values for the same compound. Agreement among the reported vapor pressure values of ethyl parathion was poor with an order of magnitude difference in values reported at the same temperature. Guckel et al. (1973) reported the vapor pressure of methyl parathion only at one temperature, i.e., 0.97×10^{-5} mmHg at 20 °C, without reference to the method used for its determination. The most frequently used value for vapor pressure of ethyl parathion, i.e., 3.7×10^{-5} mmHg at 20 °C (Bright et al., 1950), is four times greater than that reported for methyl parathion, whereas Guckel et al. (1973) found that the vaporization rate of methyl parathion was greater than that of parathion.

The wide variations in vapor pressure reported for the same compound by different authors show the need for determining vapor pressures of pesticides by a standard procedure—preferably one that relies upon a specific method for analytically determining the pesticide chemical. Measurements of vapor loss rates from surfaces under uniform conditions to establish the relationship between vapor loss and vapor pressure would be helpful in comparing relative volatility of pesticides or other potentially toxic chemicals (Spencer et al., 1973).

This paper describes procedures for determining vapor pressure and vapor loss rates of pesticides or other potentially toxic organic chemicals and reports the vapor pressure and relative volatility of ethyl and methyl parathion from glass surfaces and the vapor loss rates of methyl parathion from soils.

MATERIALS AND METHODS

Vapor Pressure. Vapor density and apparent vapor pressure were determined over the 25–45 °C temperature range using the gas saturation method (Spencer and Cliath, 1969; U.S. EPA, 1975) in which dry N₂ gas is passed through pesticide-treated quartz sand slowly enough to ensure equilibrium vapor saturation. The method was modified to include the use of polyurethane plugs as vapor traps (Bidleman and Olney, 1974), prepared as described by Turner and Glotfelty (1977). The vapor saturators, 6 × 43 cm, were made from medium-wall borosilicate glass

tubing capped with 60/50 $\bar{\text{F}}$ joints.

The treated sand for the vapor saturators was prepared by adding about 6 g of the pesticide in 100 mL of hexane to 1000 g of water-washed sand. The hexane was evaporated in an open pan and the pesticide-treated sand added to the glass column saturator. Using five saturators simultaneously, vapor pressures were measured at 25, 35, and 45 °C with the N₂ gas flow rates carefully monitored and controlled below 10 mL/min. The five saturators contained the various formulations of methyl and ethyl parathion. With ethyl parathion, both technical grade parathion (98.5%) and purified parathion (99.9%) were used; with methyl parathion, purified methyl parathion (99.9%), technical methyl parathion (80% methyl parathion, 20% xylene), and recrystallized methyl parathion (prepared by cooling technical methyl parathion until the methyl parathion crystallized and then recrystallizing the methyl parathion) were used. Since the melting point of methyl parathion is about 35 °C, additional measurements were made above and below the melting point at 30, 39, 40, and 42 °C.

The vaporized pesticides were removed from the polyurethane plugs by a 2-h Soxhlet extraction with an azeotropic mixture of hexane and acetone. The hexane/acetone extracts were concentrated to about 10 mL in a Kuderna/Danish concentrator. Concentrations of ethyl and methyl parathion in extracts were determined with a Tracor 550 gas chromatograph with a flame photometric detector. The gas chromatograph was equipped with 1.83 m X 4 mm Pyrex glass columns packed with 3% OV-1 on Chromosorb W-HP (80–90 mesh). The operating parameters were: nitrogen carrier flow, 110 mL/min; burner flow rates, 74 mL of hydrogen/min and 100 mL of air/min; with inlet, column, and detector temperatures of 200, 190, and 205 °C, respectively.

The efficiency of vapor trapping in polyurethane plugs and recovery of ethyl and methyl parathion after extraction and concentration of extracts were determined by the procedures of Thomas and Seiber (1974). Known amounts of each pesticide were vaporized from U-tubes into three polyurethane plugs arranged in series. With ethyl parathion 100% of the vapor was trapped in the first plug and recovered in the extraction, concentration, and analytical procedures. With methyl parathion the vapor was trapped in the first plug but only 90.2% of the vaporized methyl parathion was recovered in the extraction, concentration, and analytical procedures. Consequently, all data for methyl parathion are corrected for 90.2% recovery.

Vapor Loss Measurements. We measured vapor loss rates of ethyl and methyl parathion from glass surfaces and

U.S. Department of Agriculture, Science and Education Administration, and the University of California, Riverside, California 92521.

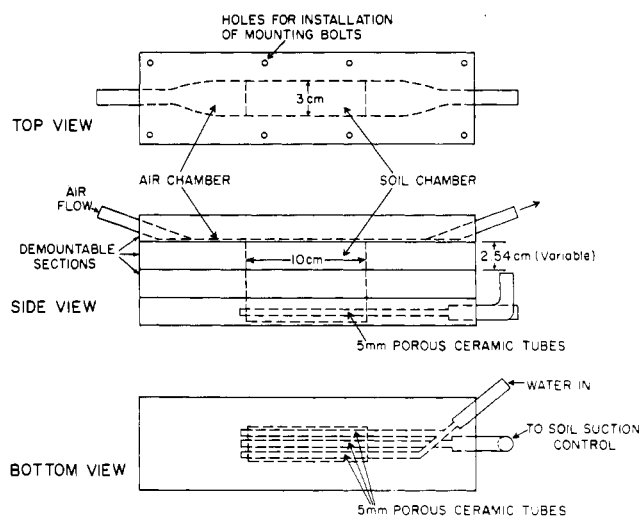


Figure 1. Schematic diagram of the volatilization chamber used for vapor loss measurements with water-control base section.

of methyl parathion from soil surfaces using an adaptation of the volatilization cell shown in Figure 1. The cell is constructed of Plexiglass with a rectangular chamber (3 cm wide by 10 cm long) for inserting soil or glass plates. The depth of the soil chamber can be varied by stacking additional center sections. Porous ceramic tubes were installed in the bottom section so we could adjust the soil-water content during volatilization measurements from soil. For measuring volatilization from glass surfaces, we used only the bottom and top sections with a glass plate inserted in a 10×3 cm recess in the bottom section. Each section of the cell is grooved for an O-ring to provide a positive liquid and vapor seal between sections. The upper section contains an air chamber (2 mm deep and 3 cm wide), which is the same width as the evaporating surface. With these dimensions, a flow rate of 1 L/min through the air chamber provides a windspeed across the vaporizing surface of about 1 km/h and changes the atmosphere in the space over the surface 167 times/min. The air chamber extends 7.5 cm on either side of the vaporizing chamber to allow air to spread out before reaching the soil or glass surface, thus providing essentially laminar air flow across the evaporating surface.

The volatilization chambers were mounted in a constant-temperature incubator as one part of the close air-flow system shown in Figure 2 with the required air flow and humidity controls so that four chambers could be used simultaneously. The vaporized pesticides were trapped in polyurethane plugs. They were extracted from the plugs and analyzed in the same manner as described

for vapor pressure measurements.

Methyl parathion vapor loss rates were measured from glass and soil surfaces using technical-grade methyl parathion and an emulsifiable concentrate formulation. The emulsifiable concentrate was Niran M-4 containing 45.7% methyl parathion, 48.2% aromatic petroleum derivatives, and 6.1% inert ingredients. Technical-grade ethyl parathion was used to measure vapor loss of ethyl parathion on glass surfaces only.

Vapor Loss from Surface Deposits on Glass Plates. Theoretically, in the case of surface deposits, vaporization of a chemical from a complete surface of constant area is independent of the depth of the chemical layer, and under constant conditions the loss rate will be constant until so little substance remains that it no longer can cover the surface. Our procedure in measuring vapor loss from glass surfaces and to eliminate adsorption effects when comparing relative volatility of chemicals was to build up and maintain a sufficient depth of ethyl and methyl parathion deposit on the glass surface so that the pesticide was vaporizing from its own surface.

The pesticides were applied to glass plates by repeatedly spraying with an atomizer. Technical-grade ethyl and methyl parathion were applied in hexane, whereas the emulsifiable concentrate of methyl parathion was applied as 1:25 dilution in water. The glass plates with the dry deposits were placed in the volatilization chambers and vaporization runs immediately started at 25 °C. The polyurethane traps were removed at intervals of 1 or 2 h for the first 5 h after initiation of the vaporization run; then an overnight interval of 17 h was followed by additional measurements at 1- or 2-h intervals. The amounts of parathion remaining on the glass plates at the end of each run were measured and added to the amounts collected in the polyurethane traps to approximate the amount of pesticide on the glass plates at the initiation of the vapor loss measurement. Two runs were made with technical methyl parathion and two with the emulsifiable concentrate; each run included four volatilization chambers. With the first run, using technical material, the N_2 gas passing over the surface was at 0% relative humidity (RH). For all subsequent measurements with ethyl or methyl parathion, the RH was adjusted to 80% to minimize adsorption of vaporized parathion on surfaces.

Vapor Loss from Soil. We measured vapor loss of methyl parathion applied to two soils as technical-grade methyl parathion and as an emulsifiable concentrate in the absence and presence of evaporating water. The two soils were San Joaquin sandy loam (Thermic Abruptic Durixeralfs) from California, with 1.24% organic matter, 9.7% clay, and a pH of 7.2, and Flanagan silt loam (Mesic Udic Haplustolls) from Illinois, with 5.1% organic matter, 25.2%

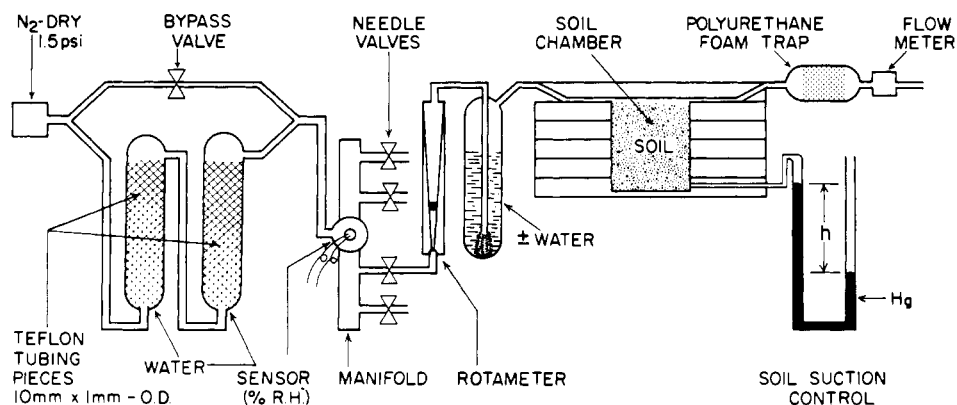


Figure 2. Schematic diagram of the gas flow system used for measuring vapor loss of pesticides from soil.

Table I. Vapor Density and Vapor Pressure of Ethyl and Methyl Parathion at Various Temperatures Measured Using Purified (99.9%) and Technical-Grade Materials

material and temp °C	no. of detn	measured temp, ^a °C	vapor density, ng/L	vapor pressure, ^b mmHg × 10 ⁻⁵
ethyl parathion				
25	11	24.9 ± 0.20 ^c	151 ± 9	0.965 ± 0.055
35	16	34.9 ± 0.10	492 ± 18	3.24 ± 0.12
45	15	45.0 ± 0.08	1838 ± 89	12.6 ± 0.62
methyl parathion				
25	12	24.9 ± 0.16	245 ± 12	1.72 ± 0.09
30	12	30.0 ± 0.12	553 ± 51	3.97 ± 0.37
35	12	34.9 ± 0.14	987 ± 67	7.20 ± 0.5
39	12	38.6 ± 0.22	1505 ± 75	11.1 ± 0.56
40	4	39.7 ± 0.22	1663 ± 183	12.3 ± 1.30
42	12	41.7 ± 0.20	2074 ± 100	15.5 ± 0.76
45	11	45.1 ± 0.12	2393 ± 282	21.8 ± 2.12

^a Temperatures measured on individual vapor saturators within the constant temperature incubator. ^b Calculated from vapor density, d , with the equation $P = d(RT/M)$ where R is the molar gas constant, T the absolute measured temperature, and M the molecular weight. ^c The 95% confidence limit or two times standard error of the mean, S_m , calculated with the equation $2S_m = 2SD/\sqrt{n}$, where SD = standard deviation, and n = number of determinations.

clay, and a pH of 5.5. Before treating soils with methyl parathion, they were autoclaved for 1 h at 16 psi and 126 °C, twice at 2-day intervals. We applied 10 ppm methyl parathion by atomizing the material onto the air-dry soil in a 10-L carboy. The technical material was applied in 15 mL of hexane and the emulsifiable concentrate in 15 mL of water to 1500 g of soil. The hexane was allowed to evaporate; then the treated soils were mixed thoroughly for 1 h in an Eberhart reciprocating shaker.

Each volatilization chamber was made up of four de-mountable sections to produce a 10 cm deep soil column. The treated soil was placed into the chambers 1 cm at a time and tamped lightly with a glass rod while the soil was wetted from the bottom through the porous ceramic tubes. Soil suction was maintained at zero tension at the bottom of the soil column. The amount of water evaporating from the soil was regulated by adjusting the RH of the N₂ gas passing over the soil surface. The RH was controlled by adjusting the proportion of the N₂ passing through the water saturators. Water loss rates were determined by measuring the amount of water added to the bottom of the column to replace that evaporated from the surface. Vapor loss of methyl parathion was measured over a 29- or 33-day period with the soil surface moist and the RH of the N₂ gas adjusted to 100% for the first few days, then adjusted to 50% RH, and subsequently back to 100% RH for the final sampling periods. Vaporization rates were measured in duplicate for each methyl parathion material on each soil at a nitrogen gas flow rate of 1 L/min at 25 °C.

RESULTS

Vapor Pressure. The vapor densities and vapor pressures of ethyl and methyl parathion at various temperatures are shown in Table I. Since we found no statistically significant differences in vapor pressure between the purified, technical, or recrystallized materials for either pesticide, all values are combined for each temperature. This indicates that it is not necessary to use purified materials when measuring vapor pressure by the gas saturation procedure if a specific method for analytically determining the trapped pesticide vapor is used.

Ethyl Parathion. The relationship between log vapor pressure and $1/T$ was linear and expressed by the equation $\log P = 12.66 - (5274/T)$, with a correlation coefficient (r) of -0.996 . The heat of vaporization ΔH_v , is 24.1 kcal/mol as calculated with the relationship $\Delta H_v = 2.303 Rm$, where R is the gas constant in calories per mole per degree, and m is the slope of the line when $\log P$ is plotted vs. $1/T$. Vapor pressures calculated from the observed vapor

Table II. Ethyl Parathion Vapor Pressures Calculated from the Observed Relation between Vapor Pressure and Temperature Compared with Previously Reported Values at Various Temperatures

temp, °C	vapor pressure, mmHg × 10 ⁻⁵				
	present study ^a	Bright et al. ^b (1950)	Williams (1951) ^c	Guckel et al. (1973)	Yang (1974)
20	0.470	3.78	1.96	0.57	0.439
25	0.942	5.97	3.51		
30	1.84	9.20	6.14		
35	3.53	13.98	10.56		
40	6.62	20.95	17.84		
45	12.18	31.02	29.66		

^a Calculated from the observed relation between $\log P$ and $1/T$, $\log P = 12.66 - (5274/T)$. ^b Calculated from Bright et al.: $\log P = 7.161 - (3395/T)$. ^c Calculated from Williams: $\log P = 10.30 - (4400/T)$.

pressure-temperature relationship over the range of temperatures from 20–45 °C are shown in Table II along with some previously reported values for the vapor pressure of ethyl parathion.

Methyl Parathion. The melting point of purified methyl parathion, measured with the Thomas-Hoover melting point apparatus equipped with a thermometer calibrated by the U.S. Bureau of Standards, was found to be 35.2–35.4 °C. Using the method of least squares to establish the best fit line with vapor pressure data for temperatures above and below the melting point resulted in two lines which intersected at 34.5 °C. Below the melting point, the vapor pressure-temperature relationship is expressed by the equation $\log P = 14.37 - (5700/T)$, with $r = -0.979$ and a heat of vaporization of 26.1 kcal/mol. Above the melting point the vapor pressure-temperature relationship is expressed by the equation $\log P = 10.61 - (4543/T)$, with $r = -0.945$ and a heat of vaporization of 20.8 kcal/mol. The difference in heat of evaporation above and below the melting point is 5.3 kcal/mol, which is considered to be the heat of fusion of methyl parathion. Methyl parathion vapor pressures calculated from our observed relationship between vapor pressure and temperature at 20, 25, 30, 35, 40, and 45 °C are 0.85×10^{-5} , 1.80×10^{-5} , 3.72×10^{-5} , 7.51×10^{-5} , 12.73×10^{-5} , and 21.5×10^{-5} mmHg, respectively. Guckel et al. (1973) reported the vapor pressure of methyl parathion was 0.97×10^{-5} at 20 °C, without indicating the method used for its determination.

Vapor Loss Rates. *Vapor Loss from Surface Deposits on Glass Plates.* Vapor fluxes of methyl parathion from

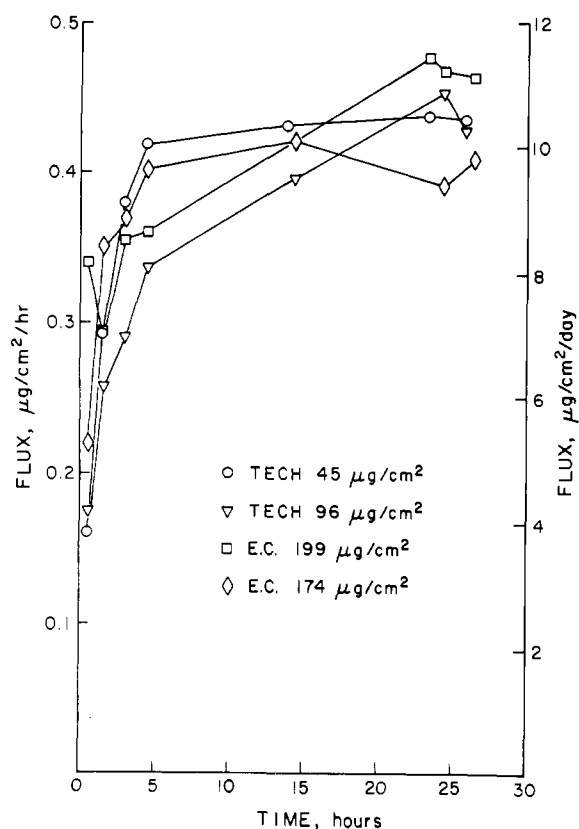


Figure 3. Methyl parathion vapor loss rates from technical-grade methyl parathion (technical) and emulsifiable concentrate (EC) on glass plates at 25 °C. Each value is an average of four replications. The values shown with the symbols are the initial deposit concentrations.

surface deposits on glass plates are shown in Figure 3. Each point represents vapor loss from four individual volatilization chambers with the data plotted at the midpoint of each time interval. The vapor loss rate initially increased with time in each case, evidently because methyl parathion vapor was being adsorbed on the walls of the volatilization chambers until the chamber walls reached some state of equilibrium with the vapor concentrations from the deposits on the glass plates. Humidifying the N₂ gas to 80% RH did not reduce or prevent this adsorption and did not seem to affect the volatilization rate.

The volatilization rate of interest, then, is that which occurs after saturation of all the vapor-adsorbing surfaces between the methyl parathion deposits and the polyurethane traps. We have assumed this rate was that measured after a maxima or a plateau in vapor-loss rate vs. time was reached. Table III summarizes such data comparing methyl parathion vapor loss rates from technical-grade and emulsifiable concentrate materials with that from technical-grade ethyl parathion. Data for vapor loss rates after 24 h (or the plateau maximum rate observed during each set of measurements) indicated no difference between the volatilization rate from technical-grade methyl parathion and from the emulsifiable concentrate formulation. From surface deposits on glass plates, the average volatilization rate after 24 h was 0.435 μg (cm²)⁻¹ h⁻¹ equivalent to 10.4 μg (cm²)⁻¹ day⁻¹ (1.04 kg ha⁻¹ day⁻¹). The vapor loss rate of ethyl parathion was about one-half that of methyl parathion, which agrees closely with their relative vapor pressures. At this rate of vaporization, most of a typical 10 μg/cm² deposit of either pesticide would volatilize within 1 or 2 days. In the case of surface deposits

Table III. Rate of Vapor Loss at 25 °C from Surface Deposits on Glass Plates When Applied as Technical-Grade and Emulsifiable Concentrate (EC) Methyl Parathion and Technical Ethyl Parathion

pesticide and source	RH of N ₂ gas, %	gas flow rate, L/min	initial deposit, μg/cm ²	vapor flux, μg (cm ²) ⁻¹ h ⁻¹
ethyl parathion technical ^a	80	1.0	298	0.210
methyl parathion technical ^a	0	1.2	45	0.434
technical ^a	80	1.2	96	0.440
technical, mean		1.2	71	0.437
EC ^a	80	1.2	199	0.465
EC ^a	80	1.0	174	0.399
EC, mean		1.1	185	0.432
Combined, Mean		1.2	129	0.435

^a Each value is an average of four replications run simultaneously. ^b Based on pesticide concentration on plate at the end of the run plus that trapped as vapor. ^c Average loss rate after 24 h of vaporization in plateau region of flux vs. time curve.

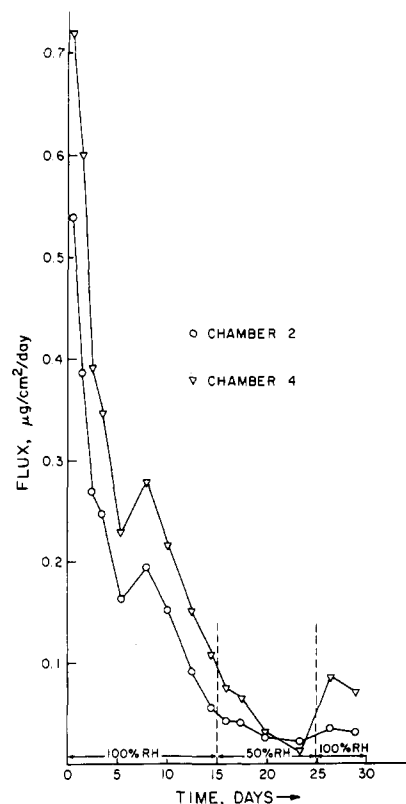


Figure 4. Methyl parathion vapor loss rates from emulsifiable concentrate (EC) incorporated into San Joaquin sandy loam as related to time and relative humidity at 25 °C.

on nonadsorbing surfaces, vapor loss rates are usually limited by the air-exchange rate. Based on the vapor pressure of methyl parathion of 1.80×10^{-5} mmHg at 25 °C, the N₂ carrier gas during the period of maximum volatilization reported in Table III was about 75% saturated with methyl parathion. This very high vapor saturation of the gas stream indicated that vapor loss rates would be much greater at higher air-exchange rates like those under field conditions.

Vapor Loss from Soil. The volatilization rate of soil-incorporated methyl parathion for the emulsifiable con-

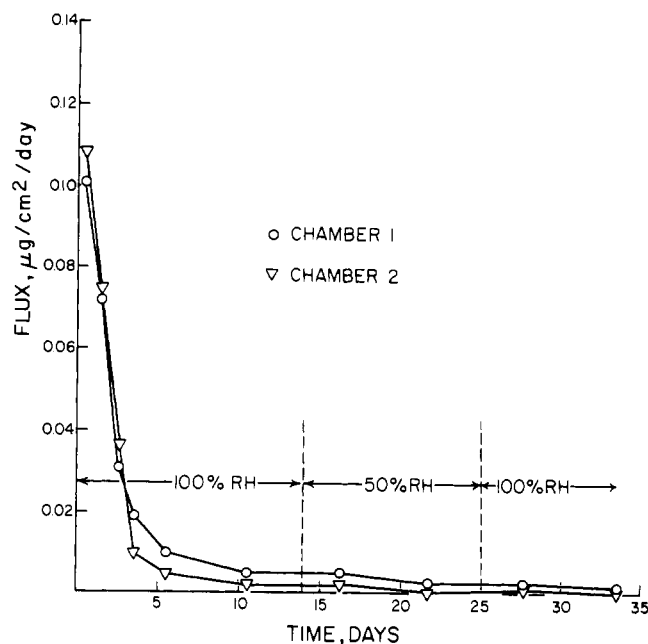


Figure 5. Methyl parathion vapor loss rates from emulsifiable concentrate (EC) incorporated into Flanagan silt loam as related to time and relative humidity at 25 °C.

concentrate formulation in San Joaquin sandy loam and Flanagan silt loam are shown in Figures 4 and 5, respectively. The vapor loss rates for the technical-grade methyl parathion were essentially the same as those for the emulsifiable concentrate in each soil. The maximum volatilization rate observed from soil-incorporated methyl parathion was $0.03 \mu\text{g} (\text{cm}^2)^{-1} \text{h}^{-1}$ ($0.72 \mu\text{g} (\text{cm}^2)^{-1} \text{day}^{-1}$) with San Joaquin sandy loam. The volatilization rate decreased rapidly with time due to a combination of surface depletion by volatilization and degradation of the methyl parathion in the soil. After 2 weeks of volatilization at 100% RH the loss rate had decreased below 0.06 and $0.005 \mu\text{g} (\text{cm}^2)^{-1} \text{day}^{-1}$ for the San Joaquin and Flanagan soil, respectively. With San Joaquin sandy loam, the total methyl parathion volatilized from the 10-cm soil columns during the 29-day period averaged 2.6% of the amount incorporated into the soil. After 29 days, only 3% of the methyl parathion remained in the soil, indicating that most of it had degraded. Methyl parathion vapor loss from Flanagan silt loam was much lower than from San Joaquin sandy loam. This probably reflected the greater adsorption of methyl parathion and faster rate of methyl parathion degradation, both due to the higher organic matter and clay contents of the Flanagan silt loam. The total methyl parathion volatilized from Flanagan silt loam averaged only 0.25% of the amounts incorporated into the soil, and after 33 days only 0.5% of the added methyl parathion remained in the soil.

Water evaporating at $0.31 \text{ mL} (\text{cm}^2)^{-1} \text{day}^{-1}$, when the carrier gas was adjusted to 50% RH, had little effect on the vaporization of methyl parathion. A more pronounced wick effect would have been expected from this relatively soluble pesticide. However, this lack of response can be accounted for by the relatively low concentration of methyl parathion remaining in the soil after 2 weeks vaporization at 100% RH and excessive drying at 50% RH which may have caused any water-transported methyl parathion to be accumulated at the surface. The fact that the volatilization rate of methyl parathion increased noticeably when the RH was increased from 50 to 100% on day 25 (San Joaquin sandy loam, Figure 4) indicates that some

methyl parathion did move to the evaporating surface by mass flow in the evaporating water and that the wick effect did contribute to the volatilization of methyl parathion from soil. This increase is caused by release of methyl parathion which moved to the surface in evaporating water at 50% RH and accumulated on the relatively dry soil surface because of restricted volatilization (Spencer and Cliath, 1973).

DISCUSSION

The fact that the technical-grade and purified materials exhibited the same vapor pressure and vapor loss rates indicates that vapor pressures can be measured by the gas saturation method using nonpurified chemicals if a specific method of determining the vaporized chemical is used to eliminate impurity effects on the vapor-pressure measurement. This fact also indicates that the vapor behavior of technical and formulated materials are similar to those for the pure chemical in both soils systems and surface deposits on nonadsorbing surfaces.

Vapor pressures and vapor losses from glass surfaces indicated that methyl parathion is about twice as volatile as ethyl parathion. This is consistent with their relative persistence on foliage, as reported by Ware et al. (1972, 1974). Our data indicated that the vapor loss from non-adsorbing surfaces was directly proportional to $P(M)^{1/2}$, as was proposed by Hartley (1969). The ratio of $P(M)^{1/2}$ for methyl and ethyl parathion is 1.81, whereas the observed ratio of the flux of methyl and ethyl parathion is 1.9 at 1.0 L/min gas flow rates.

The exact relation between volatilization rates measured in the laboratory and those expected in the field is unknown. In the field, volatilization rates from surface applications probably would be even higher than those reported herein from glass slides because of the higher rate of air exchange under most field conditions. Taylor et al. (1977) recently measured initial vaporization rates of 6.53 and $25.5 \mu\text{g} (\text{cm}^2)^{-1} \text{day}^{-1}$ of dieldrin and heptachlor, respectively, when they were applied to grass pasture at the rate of 5.6 kg/ha. Based on the dieldrin loss rate of $6.53 \mu\text{g} (\text{cm}^2)^{-1} \text{day}^{-1}$ and assuming that the vaporization rates for other compounds would be proportional to $P(M)^{1/2}$, the rate of ethyl parathion and methyl parathion loss under the same conditions would be about 10.6 and $19.3 \mu\text{g} (\text{cm}^2)^{-1} \text{day}^{-1}$, respectively. The laboratory measurements of vapor loss from glass slides along with this estimate from the field data indicate that most of a typical parathion or methyl parathion deposit on leaves would be lost by volatilization within the first few hours after application.

Vapor losses from soil-incorporated methyl parathion were much lower than from glass surfaces. Even though slightly higher vapor loss rates would be expected from methyl parathion applied directly to the soil surface than from incorporation, our data indicated that most of the methyl parathion applied to soil would be lost by degradation, rather than by volatilization. Yang (1974) similarly reported that biological degradation was the major pathway for ethyl parathion dissipation from soil.

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Isolation, Identification, and Chromatographic Characterization of Some Chlorinated C₁₀ Hydrocarbons in Technical Chlordane

Harun Parlar,* Klaus Hustert, Siegmund Gäb, and Friedhelm Korte

With the help of column chromatography, three new substances, 1-*exo*,4,5,7,8,8-hexachloro-3a,4,7,7a-tetrahydro-4,7-methanoindene (8), 1-*exo*,2-*exo*,4,5,7,8,8-heptachloro-3a,4,7,7a-tetrahydro-4,7-methanoindane (15), and 1-*exo*,2-*exo*,4,6,7,8,8-heptachloro-3a,4,7,7a-tetrahydro-4,7-methanoindane (16), were isolated from technical chlordane and were identified by spectroscopic methods (mass spectrometry, infrared, and ¹H NMR). These compounds could be synthesized by photochemical dechlorination of heptachlor (11) and of α - (or *cis*-) chlordane (17) in methanol. In addition, the mixture was investigated by capillary gas chromatography and by combined gas chromatography and mass spectrometry. The data obtained were used to characterize the composition of technical chlordane.

Technical chlordane is an insecticidal mixture of C₁₀ components formed by chlorinating chlordene (6). The earliest publications about the composition of technical chlordane deal with the isolation and identification of the main components of the mixture (Vogelbach, 1951; March, 1952; Riemschneider, 1951, 1955). Later work is concentrated mainly on the gas chromatographic separation of the mixture. Polen (1966) succeeded in characterizing 11 compounds, while Saha and Lee (1969) identified 14 different compounds. Use of the polar phases in gas chromatography led to the recognition of 26 compounds (Cochrane and Greenhalgh, 1976) and of 45 compounds (Sovocool et al., 1977) subsequently. Additional work dealt mainly with the structural elucidation of the substances isolated from the mixture (Gäb et al., 1976, 1977a,b; Cochrane et al., 1975; Wilson and Sovocool, 1977). The present paper describes the isolation, identification, and synthesis of three new chlorinated tetrahydromethanoindanes from technical chlordane. In addition an attempt is made to obtain an improved characterization of the mixture with the help of chromatographic and spectroscopic data.

MATERIALS AND METHODS

Technical chlordane, chlordene, (6), heptachlor (11), α - (or *cis*-) chlordane (17), γ - (or *trans*-) chlordane (18), α - (or *trans*-) nonachlor (23), α -chlordene (24), β -chlordene (25), and γ -chlordene (26) and also compound C (27) and

compound K (28) were kindly made available by the Velsicol Co., Chicago, Ill. Compounds 1 and 2 were prepared by photodechlorination of 4,5,6,7-tetrachloro-3a,4,7,7a-tetrahydro-4,7-methanoindene (3), which is readily obtained from tetrachlorocyclopentadiene and cyclopentadiene (Hustert et al., 1975). Compounds 4 and 5 are prepared from 4,5,6,7,8,8-hexachloro-3a,4,7,7a-tetrahydro-4,7-methanoindene (6) (Parlar, 1970). Compound 9 was obtained by Diels-Alder reaction of pentachlorocyclopentadiene and cyclopentadiene in xylene (Cochrane, 1974). 1-*exo*,4,5,6,7,8-*exo*-Hexachloro-3a,4,7,7a-tetrahydro-4,7-methanoindene (10) could be isolated in small quantities after dechlorination of heptachlor (11) with lithium aluminium hydride and cobaltous nitrate (Bieniek et al., 1970). Compound 12 was formed on reacting 4,5,6,7,8,8-hexachloro-3a,4,7,7a-tetrahydro-4,7-methanoindene-1-one with phosphorus pentachloride in carbon tetrachloride (Parlar and Korte, 1977). 4,5,6,7,8,8-Hexachloro-3a,4,7,7a-tetrahydro-4,7-methanoindane (13) was obtained by catalytic hydrogenation of 6 (Parlar and Korte, 1977), which reacted with HCl directly to β -dihydroheptachlor (14) (Falbe and Schulze-Steinen, 1966). Compound 19 was prepared by Büchel et al. (1966). Compounds 20 and 21 were obtained in minor quantities from this reaction (Gäb and Parlar, 1977). 1-*exo*,2-*exo*,3-*exo*,4,5,6,7,8,8-Nonachlor-3a,4,7,7a-tetrahydro-4,7-methanoindane (22) was isolated from technical chlordane with the help of column chromatography (Cochrane, 1974). Tables I, II, and III show the *R_f* values, relative retention times (*t_R*) relative to 4,5,6,7-tetrachloro-3a,4,7,7a-tetrahydro-4,7-methanoindene (3) and percentages of the individual compounds (determined gas chromatographically with a maximum error of $\pm 10\%$) in technical chlordane. All solvents used were of analytical reagent quality. Petroleum ether (bp 60–90 °C) was purified by distillation.

Institut für Ökologische Chemie der Gesellschaft für Strahlen- und Umweltforschung mbH München, D-8051 Freising-Attaching, Federal Republic of Germany and Institut für Chemie der Technischen Universität München, D-8050 Freising-Weihenstephan, Federal Republic of Germany.