Determination of Vapor Pressures of Some Phenoxyacetic Herbicides by Gas-Liquid Chromatography

DAVID J. JENSEN and
E. D. SCHALL
Department of Biochemistry,
Purdue University, Lafayette, Ind.

The vapor pressures of 24 esters of 2,4-dichlorophenoxyacetic acid (2,4-D) and 2,4,5-trichlorophenoxyacetic acid (2,4,5-T) have been determined using gas-liquid chromatography over the temperature range 170° to 300° C. These data were extrapolated to 25° C. in order to provide field temperature (25° C.) data for use as a criterion of herbicide volatility. The 25° C. data support the previous gage of volatility—that a phenoxy ester with five or less carbons in the ester portion is highly volatile—and indicate that the phenoxy-type herbicides with a vapor pressure greater than 1.5×10^{-4} mm. of Hg at 25° C. should be classified as "highly volatile."

THE volatility of 2,4-dichlorophenoxyacetic acid (2,4-D) and 2,4,5-trichlorophenoxyacetic acid (2,4,5-T) varies greatly with the alcohol portion of the molecule. Therefore, some of these compounds must be used with extreme caution, since they tend to vaporize and drift to adjacent areas following application.

Laboratory methods for evaluating this volatility have been helpful and several have been proposed based upon bioassay techniques (*2*, *4*, *11*, *14*) with sensitive plants. Baskin and Walker (*3*), working with tomatoes, suggested that phenoxyacetic esters containing five carbons or less in the alcohol portion were "highly volatile," while those containing more than five were "low volatile." This classification has been widely accepted and the sale of highly volatile types is prohibited in some states.

The absolute vapor pressure should also be useful in evaluating phenoxyacetic-type herbicides. Mullison and Hummer (*15*) used the Knudsen method of diffusion of the sample through a pinhole and obtained a value for the methyl ester of 2,4-D of about 1×10^{-3} mm. of Hg at 25° C. However, Gillies and Warren (*5*) using a transpiration method in conjunction with a radioisotope technique obtained a value of approximately 10×10^{-3} mm. of Hg for this compound at this temperature.

The usual methods for determining low vapor pressures have difficulties associated with the high degree of purity required. Therefore, the elimination of this requirement would be advantageous. The separation technique, gas chromatography, has been used successfully to separate these esters from each other and from impurities, and to determine physical constants. This technique thus should meet the needs for the determination of the vapor pressure of impure materials.

The validity of gas-liquid chromatography for vapor pressure determinations has not been established, although displacement analysis has been applied to vapor pressure determinations by James and Phillips (*9*) using gas-solid chromatography. A consideration of the fundamental concepts and relationships of the gas-liquid technique indicated that it should be applicable to the direct determination of vapor pressures.

The fundamental equation relating retention volume and vapor pressure, as derived by Herington (*8*), is

$$\log V_{21} = \log (p_1^\circ/p_2^\circ) + \log (\gamma_1/\gamma_2) \quad (1)$$

where V_{21} is the relative retention volume of two components, 1 and 2 (V_1/V_2), p_1° is the vapor pressure of component 1, p_2° is the vapor pressure of component 2, and γ_1 and γ_2 are the activity coefficients of components 1 and 2, respectively. Although γ can be calculated easily from the known vapor pressures and determined retention volumes, this value is not generally available and undoubtedly has slowed the application of gas chromatography to vapor pressure determinations.

This fundamental equation can be modified to give a simpler expression. The relations between retention volume and retention time were shown by Ambrose, Keulemans, and Purnell (*1*) to be

$$V_R = tF_cf = F_cf(z/u) \quad (2)$$

where V_R is the retention volume, t is time, F_c is carrier gas flow rate, f is a column pressure gradient correction, z is the distance between air and solute peaks, and u is the recorder chart speed.

With the use of relative retention volume—i.e., an internal standard—terms F_c, f, and u become common and Equation 2 reduces to

$$V_{R_1}/V_{R_2} = V_{21} = z_1/z_2 = \alpha \quad (3)$$

where α is the relative retention as used by some workers. Substituting this relationship into Equation 1 gives the expression

$$\log (z_1/z_2) = \log (p_1^\circ/p_2^\circ) + \log (\gamma_1/\gamma_2) \quad (4)$$

Equation 4 is merely a statement of the well established fact that separations in gas-liquid chromatography depend on two factors—the vapor pressure of the material and its partition coefficient in the liquid phase. If a liquid phase is selected for which separation is effected solely on vapor pressure differences, on a so-called "boiling point" column, Equation 4 reduces to

$$\log (z_1/z_2) = \log (p_1^\circ/p_2^\circ) \quad (5)$$

or

$$\alpha = z_1/z_2 = p_1^\circ/p_2^\circ \quad (6)$$

The work of Green (*6*) with simulated distillation has shown that an SE-30 silicone column does perform as a true boiling point separator and thus Equations 5 and 6 should be valid when such a column is used. His work also demonstrates that Dalton's law applies in gas chromatography as well as in other systems, resulting in the independent action of each component in the column. This independent action of each component makes it possible to determine the vapor pressures of relatively impure materials, thereby eliminating to a large extent the high degree of purification needed in other methods. In fact, the method is applicable to mixtures.

This study was undertaken to determine the vapor pressures of the normal and some branched-chain esters from methyl to octyl for 2,4-D and for 2,4,5-T, to ascertain whether any abnormalities exist in their vapor pressure relationships, and to correlate them with the results obtained previously by other methods.

Experimental

Reagents. Technical *n*-butyl and 2-ethyl hexyl esters of 2,4-D and 2,4,5-T were obtained from the Diamond Alkali Co. and purified by vacuum distillation. All other esters used in this study were prepared in this laboratory and purified by vacuum distillation. The internal standard dibutyl phthalate (DBP) and all other reagents were reagent grade. The columns were packed with silicone rubbers SE-30 and SE-52 on 60/80-mesh Chromosorb W obtained from Wilkens Instrument and Research, Inc.

Apparatus. An Aerograph Autoprep A-700 with thermoconductivity detection and copper columns was used throughout this study. The column temperature reported is the average temperature measured by using ten thermocouples (Cu-Constantan) calibrated at 0° and 100° C., which were spaced approximately equally over the length of the column and attached to it with copper wire. These thermocouples were read with a Leeds & Northrup Model K-3 potentiometer. Maximum uniformity of column temperature was obtained when the column, injector, and detector were maintained at approximately the same temperature, with the column positioned in the upper half of the oven with its axis in the vertical plane. Under these conditions temperatures were maintained to ±1° C. The recorder used was a Minneapolis-Honeywell-Brown Electronik with the input continuously variable from 1 to 20 mv. and chart speeds of 24 to 960 inches per hour in 10 steps. The 1/4-inch chromatographic columns were a 2-foot 5%, a 5-foot 20% SE-52, and a 5-foot 20% SE-30, all on 60/80-mesh Chromosorb W.

Procedure. The gas chromatographic technique employed in this study consisted of determining the retention times of the sample components at several temperatures and then expressing these times in terms of relative retention as compared to the internal standard for single ester and multiester solutions.

The internal standard DBP was chosen because its vapor pressure has been well established and falls in the middle of the series of normal 2,4-D esters. Using data from several sources which employed different methods Small, Small, and Cowley (*17*) showed the relationship between temperature and vapor pressure for this compound over the range 130° to 340° C. to be

$$\log P \text{ (mm. Hg)} = 7.065 - 1666/T - 547700/T^2 \quad (7)$$

Solutions containing a single ester were prepared for all of the esters of 2,4-D and 2,4,5-T by weighing 0.5-gram quantities of sample and DBP standard into a 5-ml. volumetric flask and diluting to volume with hexane.

Multiester solutions were prepared by weighing 0.5 gram of each of the esters and DBP into a volumetric flask and diluting to volume with hexane. A 5-ml. flask sufficed for solutions 1 to 3, but a 10-ml. flask was required for solution 4.

Table I. The Vapor Pressure of Esters at Various Temperatures

(Mm. of Hg)

Ester	Temperature, ° C. 171	187	200	225	250	275	300
			Esters of 2,4-D				
Methyl	11.0	22	35	82	170	340	580
Ethyl	8.8	18	30	70	150	290	510
Propyl	6.4	12	23	55	120	230	410
Butyl	4.5	9.2	16	41	89	180	340
Pentyl	3.9	7.7	14	32	75	160	300
Hexyl	2.1	4.5	8.1	22	52	110	220
Heptyl	...	2.9	4.8	16	40	89	180
Octyl	...	2.1	3.9	11	31	71	140
2-Propyl	7.6	17	28	65	140	270	480
2-Butyl	5.4	10	18	44	100	200	370
2-Pentyl	...	7.2	13	32	75	160	300
2-Hexyl	...	7.2	13	28	66	141	270
4-Heptyl	...	5.0	8.9	23	56	120	240
2-Octyl	...	3.1	5.4	15	40	91	180
2-Ethyl hexyl	...	2.9	5.3	15	37	85	170
			Esters of 2,4,5-T				
Methyl	6.0	14	23	55	120	230	420
Ethyl	4.9	11	19	45	98	200	370
n-Propyl	3.0	7.2	13	33	75	160	300
n-Butyl	...	4.5	8.1	25	60	130	250
n-Pentyl	...	3.9	7.0	19	46	100	210
n-Hexyl	...	2.6	4.9	14	35	81	160
n-Heptyl	...	1.8	3.4	10	30	64	130
n-Octyl	...	1.3	2.4	8.2	21	51	110
2-Ethyl hexyl	...	1.8	3.3	9.4	26	61	130

Solution 1. Methyl, 2-propyl, *n*-hexyl, *n*-heptyl, and *n*-octyl 2,4-D.

Solution 2. Methyl, ethyl, *n*-propyl, and *n*-butyl 2,4-D.

Solution 3. 2-Butyl, 2-pentyl, 4-heptyl, and 2-octyl 2,4-D.

Solution 4. All the normal esters of 2,4,5-T through octyl.

Chart measurement errors were minimized by adjusting the recorder chart speed so that the retention distance of DBP was 18 cm. or longer. This was accomplished by the injection of 1 μl. of a solution with subsequent chart speed regulation to meet this retention criterion.

The chromatography used throughout this study employed the following technique. With the carrier gas (helium) flow rate set at 60 ml. per minute the column was equilibrated, and 1 or 2 μl. of the ester solution was injected. The retention distances for the ester and DBP were measured from the initial departure from the base line of the air peak to the tip of the peak for each component. The relative retention value, α, was determined from the average of at least three separate injections and used to calculate the vapor pressure at that temperature using Equations 6 and 7.

Results and Discussion

Vapor Pressure. The vapor pressures of 24 esters of 2,4-D and 2,4,5-T determined over the range 171° to 300° C. are tabulated in Table I. Only one set of data is given because the over-all difference between the relative retentions determined using the different solution and column types was only 1%.

Table II. Gas Chromatographic and Literature Vapor Pressures for Phenanthrene at Several Temperatures

Temp., ° C.	Pressure, Mm. of Hg: Gas chromat.	Lit.
230	54	59.7
245	82	89.1
270	180	176
275	190	198

Table III. Vapor Pressure Constants for Equations of the Type log *P* (Mm. of Hg) = *B*/*T* for Some Phenoxyacetic Herbicides

Ester	2,4-D A	2,4-D B	2,4,5-T A	2,4,5-T B
Methyl	8.681	3375	8.724	3496
Ethyl	8.764	3463	8.858	3590
n-Propyl	8.931	3608	9.202	3841
n-Butyl	8.975	3690	9.679	4160
n-Pentyl	8.965	3720	9.406	4060
n-Hexyl	9.307	3987	9.631	4236
n-Heptyl	9.743	4275	9.836	4404
n-Octyl	9.786	4354	10.010	4554
2-Ethyl hexyl	9.548	4180	9.755	4374
2-Propyl	8.670	3431		
2-Butyl	8.875	3611		
2-Pentyl	9.125	3798		
2-Hexyl	8.975	3760		
4-Heptyl	9.321	3966		
2-Octyl	9.548	4220		

The fact that single and multicomponent mixtures gave essentially the same data proves that the vapor pressures of impure materials can be measured. This was further demonstrated by chromatographing a solution of a commercial formulation of the iso-octyl esters of

Table IV. Comparison of 25° C. Vapor Pressures by Three Methods

Ester	Vapor Pressure, Mm. of Hg × 10^3 Knudsen (15)	Gas chromat.	Transpiration (5)
Methyl	1.55	2.3	12.7
Ethyl	0.86	1.1	11.5
Isopropyl	1.2	1.4	10.5
n-Heptyl	...	0.02	1.35

Table V. Observed and Calculated Vapor Pressure of Methyl 2,4-D

Temp., ° C.	Pressure, Mm. of Hg Obsd.	Calcd.
130	1.9	2.0
140	3.1	3.2
150	4.5	5.1
160	8.0	7.7
170	12	12
200	35	35
250	170	170
275	340	330

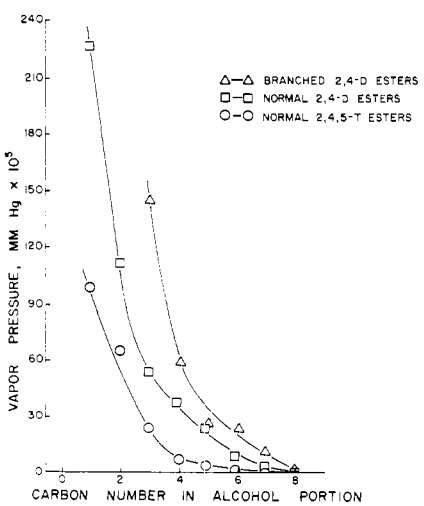

Figure 1. Vapor pressures of esters of 2,4-D and 2,4,5-T at 25° C.

2,4-D and 2,4,5-T to which methyl 2,4-D and 2,4,5-T and DBP had been added. Even though oils and emulsifiers normally present in this commercial product had not been removed, the relative retention ratios obtained were identical with those obtained with single ester solutions.

The weight ratio of the ester to the standard (DBP) in the sample solution appears to be relatively unimportant. This was confirmed by the fact that ratios of 1:3 to 3:1 did not result in significant differences, as evaluated with the methyl ester of 2,4,5-T. It was also confirmed using a compound of established vapor pressure—e.g., anthracene. Even though the solubility of anthracene in hexane was so low that a DBP–anthracene ratio of 50 to 1 was obtained in the test solution, the observed vapor pressure of 182 mm. of Hg at 275° C. agrees well with that reported for anthracene: 187.3 mm. of Hg (*16*).

The size of the sample chromatographed also appears to be relatively unimportant. Injections of 0.2 to 10 μl. did not result in significant differences when evaluated with *n*-butyl and 2-butyl 2,4-D.

To estimate the reliability of the vapor pressures obtained by this method the vapor pressure of a compound with well established vapor pressure data, phenanthrene, was determined at several temperatures and compared with literature values (*10*) (Table II). The average difference between the two sets of data was 6 mm. of Hg, which supports the ability of this method to give valid vapor pressures within the limit of experimental error.

For practical applications, vapor pressure data at ordinary field temperatures (25° C.) were of primary interest. Since these esters could not be chromatographed at this low temperature and their pressures calculated directly, the validity of extrapolating higher temperature data to these conditions was investigated.

Examination of the pressures obtained at seven temperatures over the range of 171° to 300° C. (Table I), when plotted in the familiar log P *vs.* $1/T$ manner, showed these data to be linear, as has been shown for other materials (*7*, *13*, *18*). Therefore, equations of the form $\log P = A - B/T$ were determined using linear regression analysis (Table III).

The 25° C. vapor pressures calculated from the equations for 24 esters ranged from 230 to 0.54 × 10^{-5} mm. of Hg for the most volatile (methyl 2,4-D) to the least volatile (*n*-octyl 2,4,5-T), respectively. The vapor pressures of methyl, ethyl, and 2-propyl 2,4-D determined by this procedure are very close to those of Mullison and Hummer (*15*) (Table IV) and the vapor pressure range obtained for methyl to *n*-heptyl 2,4-D is much greater than that determined by Gillies and Warren (*5*).

The extrapolation from 171° to 25° C. is rather extensive, but there is evidence supporting its validity. The methyl 2,4-D vapor pressures determined over the range 130° to 170° C. on a 2-foot SE-52 column agree with those calculated from the straight-line equation (Table V) derived from data obtained over the 171° to 300° C. range. Thus, the validity of extrapolation to 130° C. is verified. Further evidence supporting the extrapolation comes from the agreement of the calculated vapor pressures with those obtained at 25° C. by previous methods (Table IV), particularly the Knudsen method. These data confirm the feasibility of extrapolation to 25° C.

Volatility Criterion. A plot of the vapor pressure *vs.* the number of carbons in the alcohol portion for the normal esters of 2,4-D (Figure 1) supports the proposal of Baskin and Walker (*3*) to locate the point of division into the "highly volatile" and "low volatile" classification between five and six carbons. The pressure increases abruptly below the six-carbon point at 25° C.

The branched-chain esters, as expected, were more volatile than the corresponding normal compounds. In fact, it would appear from these data (Figure 1) that even the branched six-carbon ester of 2,4-D should be included in the highly volatile group, since its pressure corresponds to that of the normal pentyl derivative.

The data for the normal 2,4,5-T esters show these to be less volatile than the corresponding 2,4-D compounds. The curves (Figure 1) indicate that the break occurs between three and four carbons and, on this basis, the *n*-butyl ester should fall into the low volatile group. This is in conflict with the classification of Baskin and Walker (*3*) based on tomato bioassay. However, in a study of 44 species of weeds, Linser (*12*) found the average effectiveness of butyl 2,4,5-T to be 1.43 times that of the 2,4-D derivative. This greater toxicity undoubtedly contributes to the difference, but is not sufficient to classify this compound in the highly volatile group.

Conclusions

On the basis of the data presented in Figure 1 and the classification of Baskin and Walker (*3*) it would appear that 2,4-D and 2,4,5-T derivatives with a vapor pressure greater than 1.5 × 10^{-4} mm. of Hg at 25° C. should be classified as highly volatile. The variation in species susceptibility would need to be considered in specific cases but as a general rule these data indicate that the highly volatile designation is appropriate for those phenoxyacetic herbicides exceeding this value.

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HERBICIDE ABSORBANCE

Interaction of Ethyl *N,N*-Di-*n*-propylthiolcarbamate (EPTC) with Montmorillonite

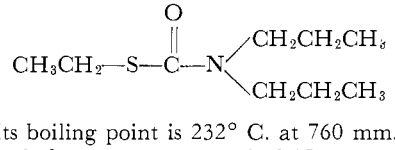
M. M. MORTLAND and W. F. MEGGITT

Departments of Soil Science and Crop Science, Michigan State University, East Lansing, Mich.

Results of infrared studies of EPTC-montmorillonite complexes show a decrease in the CO stretching and an increase in the CN stretching frequencies indicating coordination of the EPTC to the exchangeable metal ion through the oxygen of the carbonyl group. The amount of shift was determined by the kind of metal ion on the exchange complex. The EPTC-montmorillonite complexes were stable against atmospheric humidity but, when immersed in water, the EPTC could be completely displaced. Bioassay showed that EPTC-montmorillonite complexes exerted herbicidal activity against germination and growth of rye grass.

THE LITERATURE concerned with the interaction of organic pesticides and soil colloids has been reviewed recently by Bailey and White (*1*). Considerable work has been done in investigating the various factors affecting adsorption of various pesticides such as pH, moisture content, kind of exchangeable ion, nature of clay mineral, and effect of organic matter. However, relatively little has been reported on the status of the adsorbed molecule concerning exactly what sort of interaction exists between the adsorbent and the adsorbate. Infrared absorption provides a tool which can often establish such interactions as hydrogen bonding, coordination, salt formation, and actual breakdown or conversion of the compound to other forms. The work reported here is concerned with the mechanism of adsorption of ethyl *N,N*-di-*n*-propylthiolcarbamate (EPTC) by montmorillonite, a clay mineral of high specific surface (800 sq. meters per gram), as revealed by infrared absorption.

The EPTC compound is a selective herbicide especially active against annual grasses and certain broadleaf weed species. The structural formula is:



Its boiling point is 232° C. at 760 mm., and the vapor pressure is 0.15 mm. at 25° C. The solubility in water is 375 p.p.m., and it is miscible in such organic solvents as benzene, toluene, xylene, acetone, methanol, and 2-propanol.

Methods

The montmorillonite used in this study was H-25 from Upton, Wyo., supplied by Wards Natural Science Establishment. Homoionic clays were prepared by treating the <0.5-micron fraction with chloride salts of the various cations in excess of the exchange capacity. After flocculation had occurred, the supernatant liquid was siphoned off, distilled water was added to bring it to the original volume, and the chloride salts were added again. This process was repeated three times at the end of which no more salts were added, but the clays were allowed to settle and were redispersed with distilled water until the clays showed signs of not reflocculating, at which time they were placed in dialysis bags and dialyzed against distilled water until the conductivity of the dialyzate approached that of distilled water.

Thin films (2 to 5 mg. per sq. cm.) of montmorillonite were prepared by evaporating in dishes of aluminum foil. The films, which could be readily stripped from these surfaces, were placed in a vacuum desiccator containing a dish of liquid EPTC. The desiccator was evacuated with a rotary pump for an hour, the stopcock to the vacuum line closed off, and the samples were allowed to adsorb EPTC from the gaseous state provided by the vapor pressure of the liquid EPTC. Five days were apparently sufficient to give maximum adsorption since liquid as well as complexed EPTC was noted in the infrared spectra after this period. Infrared spectra were obtained by mounting the films at right angles to the beam in a Beckman IR-7 spectrophotometer.

Infrared Spectra of EPTC-Montmorillonite Complexes

Figure 1 shows the infrared spectra of EPTC complexed with montmorillonite of varying cation saturation in the region 1150 to 1750 cm.$^{-1}$ The top spectrum is that of pure liquid EPTC. Great changes in the spectra of the compound are indicated. The intense peak at 1655 cm.$^{-1}$ in the liquid is the carbonyl stretching band which shifts to much lower frequencies upon complexation with montmorillonite. The peak at about 1630 cm.$^{-1}$ is the deformation band for water. This figure shows that the amount of shift is a function of the kind of metal ion on the clay exchange sites. There is a relationship between the amount of shift of the carbonyl stretching band and the known complexing abilities of the various ions; copper, aluminum, and cobalt cause a greater shift than the alkali metal and alkaline earth cations represented. The band at 1222 cm.$^{-1}$ is allocated mostly to C—N stretching in accordance with the observations of Nyquist and Potts (*6*) in their work on thiocarbamates where they reported this strong band in the 1152 to 1275 cm.$^{-1}$ region. The