

Codistillation of DDT with Water

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The codistillation rate of DDT with water from a placid surface in $\mu\text{g.}$ of DDT per gram of water parallels concentration from 1 to at least 100 p.p.b. at 25°, 30°, and 35° C. At the highest concentrations tested in this study, the codistillation rate was as much as six times greater than that which would be anticipated on the basis of the Rassow-Schultzky equation. This finding is in line with DDT's great affinity for the air-water interface, which facilitates the high codistillation rate. The significance of these results as related to the practical use of DDT is discussed.

AN INVESTIGATION of the factors responsible for the odd results obtained with aqueous DDT suspensions in mosquito-larvae bioassays demonstrated that DDT was heterogeneously distributed in 10 p.p.b. (parts per billion) aqueous suspensions and that DDT codistilled with water, more than 50% of it being volatilized from a 10 p.p.b. suspension in 24 hours at room temperature (3). Although these fundamental findings were unexpected, they are consistent, at least qualitatively, with the physico-chemical considerations that one would expect to govern the volatilization rate of DDT with water. For example, it was possible to determine quantitatively and with close precision the codistillation rate of DDT with water at the boiling point of water. However, the volatilization of DDT from a boiling, aqueous DDT suspension, which is being churned to uniformity, cannot be compared with that which takes place at ambient temperatures from a placid surface.

It became of interest to the authors to determine this codistillation rate of DDT with water (from water and acetone-water suspensions) since in actual practice DDT in the presence of evaporating water would generally be volatilized from a placid surface. This information of the world's most widely used insecticide may be of practical importance and point the way to its more efficient utilization. It may also provide an insight into the mechanism of DDT's disappearance from various media.

On the basis of the authors' original experiments (3), a loss of DDT, amounting to more than 50% from a 10 p.p.b.

suspension in 24 hours, was believed to be so great because the concentration of the suspension was so extraordinarily dilute and a minute loss was an appreciable part of the whole; further, that the high affinity of DDT for the periphery of the liquid, specifically for the upper surface, facilitated its loss. (The term "concentration" as here used means the weight of DDT per unit weight of suspension. This use of "concentration" is unconventional since the DDT is heterogeneously distributed, but no better term is available.) However, no one had determined by actual measurement what the loss of DDT from a placid surface would be when a series of its concentrations were exposed. This paper reports on the results of such experiments at 25°, 30°, and 35° C.

Experimental

Aqueous Dispersions. Appropriate aliquots of acetone containing *p,p'*-DDT-4-C¹⁴ (2.1 $\mu\text{c.}$ per mg.), kindly furnished by P. A. Dahm, of Iowa State College, and used by authority of the U. S. Atomic Energy Commission, were added to pint glass jars. After the acetone was removed by evaporation, 250 ml. of distilled water was added to each jar giving a range of concentrations from 0.36 to 81 p.p.b. The jars were sealed and heated at 90° to 100° C. with frequent shaking for 1 hour and then equilibrated in a water bath at 25°, 30°, or 35°, all $\pm 0.5^\circ$ C. The jars were shaken vigorously, opened, weighed, and returned to the water bath. After 24 hours, they were reweighed, and the water lost by evaporation was calculated.

The residual radioactivity was determined by the method described previously (3).

Aqueous-Acetone Dispersions. Acetone solutions (1.25 ml.) that contained various quantities of *p,p'*-DDT (m.p., 106–107° C.) or of the C¹⁴-DDT were added to separate pint jars containing 250 ml. of distilled water. The dispersions were stirred with a glass rod, weighed, and placed in a water bath at 25° C. for 24 hours. Finally the jars were removed, reweighed, and the DDT remaining in each jar was analyzed either radio-metrically or spectrophotometrically by the method already cited.

Results

The results of the experiments are given in Table I. Figure 1 illustrates graphically how the rate of codistillation ($\mu\text{g.}$ of DDT per gram of H₂O, hereafter called the DDT codistillation rate) varies with the initial DDT concentration. Because the ranges covered by the two variables in Figure 1 are so great, the data are plotted on a log-*vs.*-log basis. The straight lines obtained at three different temperatures with concentrations below 100 p.p.b. indicate that there is a direct relationship between initial DDT concentration and the DDT codistillation rate.

The DDT codistillation rate is calculated from a 24-hour test period and is therefore an average value. The instantaneous rate of loss necessarily must be much higher than the average rate being reported, especially since less than half of the DDT remained at the

end of the test period in all instances. Were instantaneous rates available, they would probably be in line with first-order kinetics.

The experiments were performed at different times, e.g., those at 25° C. at three different times, and differences in humidity and air movement undoubtedly account for the large variation in loss of water from these systems. However, as may be seen from Figure 1, the DDT codistillation rate did not show much deviation from the straight-line relationship below 100 p.p.b. in spite of the different water losses and the different times of test.

The accuracy of determining by spectrophotometric analysis the amount of DDT lost from 300 to 1000 p.p.b. concentrations at 25° C. was subject to considerable error since the percentage of change in concentrations during the 24-hour interval was small. When the average values for the DDT and water lost from these concentrations were substituted in the Rassow-Schultzky (7) equation to calculate the vapor pressure of DDT at 25° C., a value of 1.9×10^{-6} mm. was obtained. This value is almost six times the 3.4×10^{-7} mm. reported by

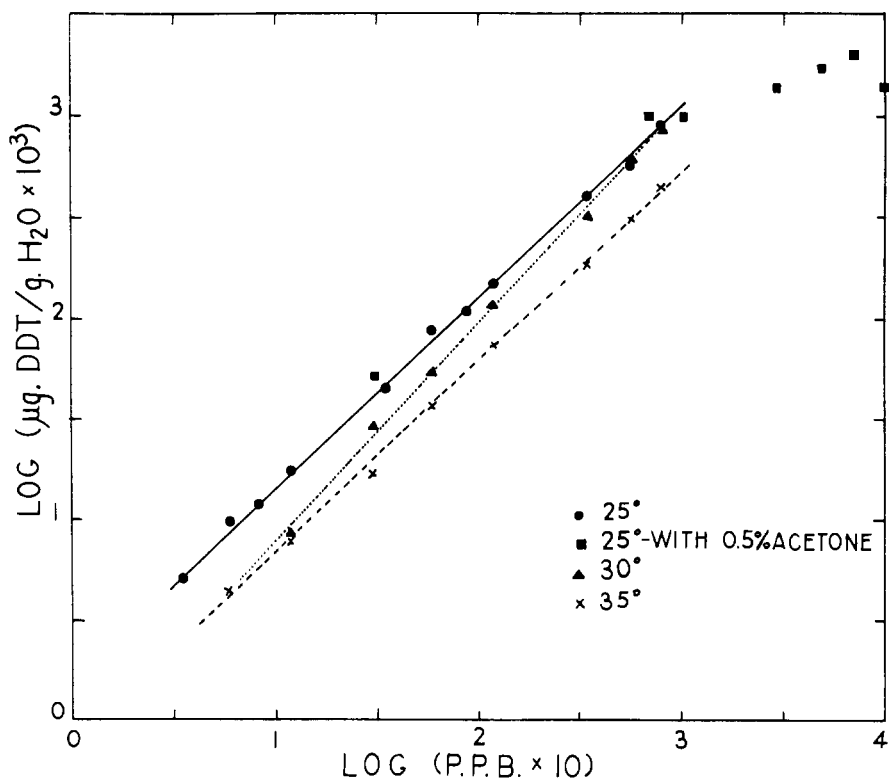


Figure 1. Codistillation of DDT with water at 25°, 30°, and 35° C.

Table I. Volatilization of DDT from Aqueous Suspensions at 25°, 30°, and 35° C., and from Aqueous-Acetone Suspensions at 25° C.

Temp., °C.	Initial Conc. of DDT, P.P.B.	DDT Present Initially, μG.	DDT Recovered After 24 Hr., μG.	DDT Lost During 24 Hr., μG., Calcd.	Water Lost During 24 Hr., Grams	% DDT Lost	μG. DDT Lost per Gram Water	% DDT Lost per Gram Water	
ULTRAVIOLET ANALYSES ^a									
25	1000	250	232	18	12.6	7.2	1.4	0.6	
	700	175	151	24	12.2	13.7	2.0	1.1	
	500	125	104	21	12.7	16.8	1.7	1.3	
	300	75	58	17	12.5	22.7	1.4	1.8	
	100	25	12	13	12.6	52.0	1.0	4.1	
RADIOMETRIC ANALYSES									
25	81	20.2	7.6	12.6	14.1	62.4	0.89	4.4	
	70 ^a	17.5	8.2	9.3	9.3	53.1	1.0	5.7	
	58	14.4	6.6	7.8	13.6	54.2	0.57	4.0	
	35	8.7	3.4	5.3	13.4	60.9	0.40	4.5	
	12	3.0	0.88	2.1	14.0	70.0	0.15	5.0	
	8.0	2.0	0.49	1.5	14.2	75.0	0.11	5.3	
	6.0	1.5	0.33	1.2	14.0	80.0	0.086	5.7	
	3.6	0.89	0.21	0.68	14.8	76.4	0.046	5.2	
	3.2 ^a	0.80	0.32	0.48	9.2	60.0	0.052	6.5	
	1.2	0.30	0.06	0.24	14.4	80.0	0.017	5.6	
	0.84	0.21	0.06	0.15	13.0	71.5	0.012	5.5	
	0.60	0.15	0.03	0.12	12.4	80.0	0.0096	6.5	
	0.36	0.09	0.02	0.07	13.5	77.7	0.0052	5.8	
	30	79	19.7	8.41	11.3	13.4	57.4	0.844	4.27
		56	14.0	3.50	10.5	17.9	75.0	0.586	4.2
34		8.5	2.87	5.6	17.6	65.9	0.317	3.7	
11.6		2.9	1.06	1.8	15.6	62.1	0.115	4.0	
5.8		1.4	0.366	1.0	18.7	71.4	0.054	3.8	
3.1		0.78	0.295	0.48	16.4	61.5	0.030	3.75	
1.16		0.29	0.144	0.15	17.5	51.7	0.0086	2.95	
35		79	19.7	5.33	14.4	32.7	73.2	0.440	2.24
		56	14.0	4.1	9.9	31.4	70.6	0.315	2.25
	34	8.5	2.6	5.9	32.7	69.4	0.180	2.14	
	11.6	2.9	0.62	2.3	32.3	79.3	0.071	2.45	
	5.8	1.4	0.26	1.1	30.8	78.5	0.036	2.55	
	3.1	0.78	0.18	0.60	32.5	77.0	0.018	2.37	
	1.16	0.29	0.04	0.25	31.8	86.1	0.008	2.71	
0.59	0.149	0.023	0.126	28.4	84.6	0.001	2.96		

^a Aqueous-acetone suspensions.

Balson (7) for the vapor pressure of DDT at 25° C.

Data in the 1 p.p.b. range were collected close to the limit of measurement and will therefore be less accurate than the other radiometric analyses.

The fact that some of the dispersions were aqueous-acetone seems to have had no great effect on the codistillation rate. Loss of weight from acetone-water suspensions was calculated as water loss, and a small error may be involved here. The authors' interest in the codistillation of DDT from aqueous-acetone dispersions stems from the use of this dispersion in bioassays on mosquito larvae. Aqueous-acetone is not normally used to apply DDT, and the data are therefore of academic rather than of practical interest.

Discussion

If DDT behaves ideally in solution, the codistillation rate of DDT should increase proportionately with its concentration up to its saturation point (Raoult's Law); above saturation the rate should remain constant because the undissolved DDT would be in the bulk of the liquid rather than on the upper surface, the only surface from which volatilization can occur. But the authors' findings did not support the assumption that DDT behaves ideally since the codistillation rate of DDT with water proved to be roughly proportional to the DDT concentration up to about 100 p.p.b. This figure is far above the solubility value (saturation point) of 1.2 p.p.b., recently determined in this laboratory (2).

For a logical explanation of these results, we must fall back on the demonstrated heterogeneity of DDT suspensions and the particular affinity of DDT for the upper surface of the liquid. Since DDT accumulates on the upper surface, from whence it can volatilize far more readily than if it were uniformly distributed in the aqueous dispersion, it follows from the colligative nature of vaporization from liquid systems that the codistillation rate should exceed that which may be calculated from the Raszow-Schultzky (6) equation. At the 100 p.p.b. level, the rate was almost three times greater than the calculated value; at the 300 to 1000 p.p.b. level, it was on the average almost six times greater. However, the codistillation rates are still roughly in the same order of magnitude as the value calculated from the equation and therefore not inconsistent with it. The extreme hydrophobic nature of DDT, and its consequent heterogeneity in aqueous suspension, accounts for DDT's atypical behavior.

The effect of temperature on the DDT codistillation rate is interesting. The amount of DDT codistilling per gram of water according to the Raszow-Schultzky (6) equation given below

$$\frac{W_{\text{DDT}}}{W_w} = \frac{M_{\text{DDT}} \times P_{\text{DDT}}}{M_w \times P_w}$$

W = wt. of distillate
 M = molecular weight
 P = vapor pressure
 w = water

depends on the ratio of vapor pressure of DDT to that of water at the different temperatures. Substituting these values [P_{DDT} from Balson (7)] in the equation, we obtain:

at 25° C., 0.282 $\mu\text{g. DDT/gram H}_2\text{O}$
30° C., 0.465 $\mu\text{g. DDT/gram H}_2\text{O}$
35° C., 0.747 $\mu\text{g. DDT/gram H}_2\text{O}$

It appears from these figures that the codistillation rate of DDT should increase almost three times when the temperature increases from 25° to 35° C. But the data show that the rate decreases in this temperature interval. A possible explanation for this anomaly is the greater thermal agitation of the water molecules and DDT's increased solubility with increasing temperature. These effects would tend to diminish the accumulation of DDT at the air-water interface and thereby lessen the codistillation rate. At first, the authors had not considered these effects of increased temperature.

Although the codistillation rate of DDT decreased with increasing temperature between 25° and 35° C., the water loss increased (averaged 13.8 grams at 25°, 16.7 at 30°, and 31.6 at 35°), and the net result was an increasing weight of DDT codistilling per 24-hour period with increasing temperatures.

Practical Considerations

The DDT-water codistillation phenomenon adds another dimension to the picture describing the loss of DDT from various media. For example, DDT applied to a wool garment will protect against insects for several years (5), but applied to livestock it will not protect more than several weeks (4). Although the insecticide on an animal is known to be absorbed, metabolized, stored, excreted, and otherwise dissipated, some of the DDT undoubtedly volatilizes with water vapor emitted through the skin of the animal. For example, the water vapor lost from a lactating cow at 25° C. has been reported to be about 35 pounds per day per 1000 pounds of body weight (12), the greatest percentage of these losses occurring from the outer body surfaces (at least 80% at high temperatures). Similarly, soil is known to volatilize considerable quantities of water, and over a period of time the loss of DDT codistilling by this route may be considerable.

These examples are indicative of how codistillation may operate, but they do not establish the role of codistillation losses in its proper perspective, and this should be done. Under precise conditions, it is possible to predict the loss

of DDT from a laboratory test container and qualitatively, at least, predict the effects of the loss in, let us say, a mosquito-larvae bioassay. The authors' colleagues at the Orlando, Fla., laboratory of this Division have amply demonstrated with biological tests the effects of DDT's codistillation and heterogeneity in suspension (7, 8, 10, 11). They have shown that these factors must be considered in bioassays with DDT. However, estimation of codistillation losses in a less controlled practical situation would undoubtedly be subject to much error. Such a situation is to be expected since dissipation of DDT or any insecticide from soil, to cite a practical situation, is a complex problem and may be influenced by many variables, e.g., decomposition, erosion, sorption (9), temperature, rainfall, sun exposure, humidity, type of soil, as well as accompanying ingredients in the formulation applied. At our present stage of knowledge, each situation has to be studied individually to determine how great a part codistillation plays.

The fact that we are aware of codistillation will enable us to seek means to employ or avoid it in planning for the more efficient utilization of an insecticide. For example, the long-chain alcohols, which act as water-evaporation retardants, may extend the effectiveness of DDT when codistillation of this insecticide occurs. In some applications, water can be excluded to avoid codistillation. Another point worth considering with the persistent insecticides is that codistillation losses may be very small over a period of a day or two, yet over a period of months or years, they may become appreciable.

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Received for review August 2, 1962. Accepted November 2, 1962.