

## Diffusion of Stabilizers in Polymers. IV. 2,4-Dihydroxybenzophenone in Plasticized Poly(vinyl Chloride)

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### Synopsis

The diffusion of the radioactively labeled ultraviolet stabilizer 2,4-dihydroxybenzophenone in compression-molded sheets of plasticized poly(vinyl chloride) was studied over the temperature range of 30°–75°C. No detectable diffusion occurred in the 0% and 10% plasticized poly(vinyl chloride) when the diffusion temperature was below the glass transition temperatures of the polymers. Diffusion coefficients have been measured for plasticizer concentrations of 20, 30, 40, and 50 wt %. In each case, the variation of the diffusion coefficient  $D$  with temperature  $T$  can be represented by an Arrhenius expression  $D = D_0 \exp(-E/RT)$ . The linear relation  $\log D_0 = -7.1 + 0.20E/T$  was obtained as an empirical expression of the results.

### INTRODUCTION

Previous papers in this series reported on the diffusion of hydroxybenzophenones in polyolefins<sup>1,2</sup> and polyurethanes.<sup>3</sup> The experiments were performed at temperatures within the range of 36°–75°C, which were well above the glass transition temperatures ( $T_g$ ) of the polymers.

The glass transition temperature of poly(vinyl chloride) can be readily altered from around 80°C down to -50°C by the incorporation of a suitable concentration of a plasticizer.<sup>4</sup> These changes in glass transition temperature will influence the rate at which other additives (e.g., UV stabilizers, antioxidants, HCl absorbers) diffuse within the polymer. Diffusion can be important in controlling the retention of additives in polymers<sup>5,6</sup> and also in determining the ability of a stabilizer molecule to diffuse to reactive sites, which are, for example, in the surface layers of polymers,<sup>7</sup> so that the incorporation of a plasticizer into PVC may affect the efficiency with which additives stabilize the polymer.

The present paper reports the results obtained for the diffusion of 2,4-dihydroxybenzophenone, a UV stabilizer, in PVC plasticized with various concentrations of a phthalate ester. The experiments were carried out within the range of 30°–75°C, which meant that in most cases the experimental temperature was above the  $T_g$  of the polymer, but in some cases it was below the  $T_g$  of the polymer.

## EXPERIMENTAL

### Materials

**Ultraviolet Stabilizer.** The preparation and purification of the  $^{14}\text{C}$ -labeled sample of 2,4-dihydroxybenzophenone have been reported previously.<sup>1</sup>

**Plasticizer.** The plasticizer used was a commercial sample (Shell Chemicals (UK) Limited) of the phthalate of Linevol 79. Linevol 79 is a blend of predominantly (>80%) linear  $\text{C}_7$ ,  $\text{C}_8$ , and  $\text{C}_9$  alcohols.

**Polymer.** An atactic, commercial-grade PVC resin (Breon S.125/12, BP Chemicals Limited) in the form of a white powder was used throughout this work.

### Formation of Polymer Sheets

Sheets of PVC were prepared with plasticizer at concentrations of 0, 10, 20, 30, 40, and 50 wt %.

The various compositions of plasticizer and PVC powder were made up together with 2% of a barium/cadmium/zinc stabilizer system and 0.5% stearic acid as a lubricant, initially mixed by hand and then thoroughly mixed for 4 min at a temperature of 155°C on a two-roll mill (D. Bridge and Co. Limited) before being calendered to sheets with thicknesses of  $\sim 0.14$  cm.

Disks (3.5 cm in diameter) of the polymer were cut from sheets prepared by pressing 7 cm  $\times$  7 cm square pieces (one or more depending on the thickness required) of the calendered sheets between two sheets of mold release paper using a compression molding machine. This technique has already been described in detail.<sup>3</sup> The molding conditions used varied somewhat with the plasticizer concentration, and these conditions are shown in Table I. The sheets were cooled ( $\sim 25^\circ\text{C}/\text{min}$ ) to room temperature while under pressure by passing water through the platens.

### Glass Transition Temperature and Density Measurements

The glass transition temperatures of the PVC samples were measured to an accuracy of  $\pm 5^\circ\text{C}$  using a differential scanning calorimeter (Perkin-Elmer

TABLE I  
Compression Molding Conditions

Plasticizer, wt %	Thickness of sheet, cm	Mold temper- ature, $^\circ\text{C}$	Mold pressure, tons on 4-in.- diam. ram	Preheat time, min	Compression time, min
0	0.02-0.03	175	12	5	3
10	0.02-0.03	170	12	5	3
20	0.06-0.10	167.5	15	5	3
30	0.14-0.20	162.5	15	5	3
40	0.16-0.22	157.5	15	6	3
50	0.20-0.22	150	15	6	3

TABLE II  
Polymer Properties

Plasticizer, wt %	Glass transition temp., °C	Density, g/cm <sup>3</sup>
0	76	1.41
10	57	1.36
20	43	1.31
30	27	1.27
40	10	1.21
50	-15	1.17

DSC-1B, Norwalk, Connecticut, U.S.A.). These results are shown in Table II together with the value of the densities of the polymers which were obtained by weighing several disks of each of the polymers in air and water.

### Determination of Diffusion Coefficients

The apparatus and procedure have been described elsewhere.<sup>1</sup> The experiments were carried out in the temperature range of 30°–75°C with disks of the polymers whose thicknesses were such that the equilibrium counting rates were reached after between 40 and 1500 hr. The 2,4-dihydroxybenzophenone was as usual applied to the polymer disks as a standard solution in acetone. Amounts were used which gave final equilibrium counting rates of between 100 and 250 counts/min. These amounts were very similar to those used for the experiments

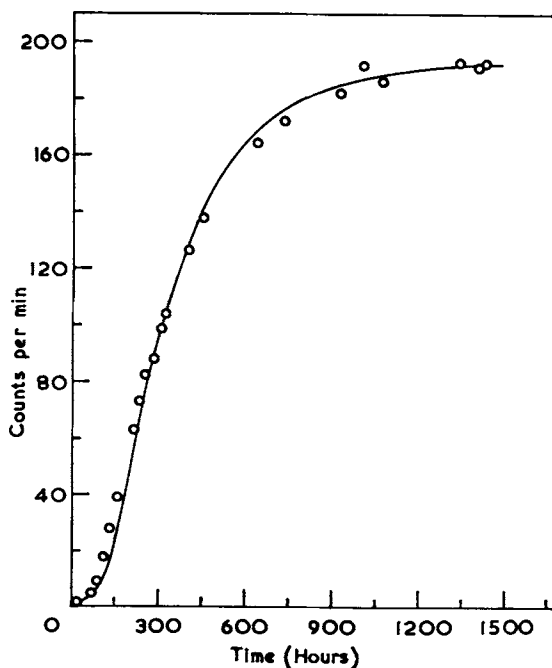


Fig. 1. Variation in surface counting rate for diffusion in 30% plasticized PVC: temperature, 40°C; disk thickness, 0.142 cm; (○ ○ ○ ○) experimental points; (—) theoretical curve for  $D = 2.54 \times 10^{-9}$  cm<sup>2</sup>/sec.

TABLE III  
 Arrhenius Parameters for Diffusion

Plasticizer, wt %	$D_0$ , $\text{cm}^2/\text{sec}$	Activation energy, kcal/mole
20	$5.9 \times 10^9$	27.9
30	3.5	13.1
40	$3.3 \times 10^{-2}$	9.1
50	$1.7 \times 10^{-3}$	6.9

with polyurethanes<sup>3</sup> for polymer disks of equivalent thicknesses. It was shown<sup>3</sup> that the polyurethanes were not saturated with the stabilizer at concentrations corresponding to these counting rates. It is, therefore, unlikely that the PVC samples were saturated at these concentrations of the stabilizer. This was confirmed by doubling the amounts of stabilizer applied to disks with the various plasticizer concentrations and following the diffusion at the lowest temperature studied. The equilibrium counting rates in all these cases were double those previously recorded, which confirmed that saturation of the polymer disks did not occur. The diffusion equation which corresponded to nonsaturation conditions<sup>1</sup> was, therefore, used to evaluate the diffusion coefficients throughout the present work.

## RESULTS AND DISCUSSION

The theoretical diffusion equation requires a value of the absorption coefficient of the polymer for the <sup>14</sup>C beta particles. This was obtained<sup>1</sup> from the value of the density of the polymer shown in Table II.

Diffusion studies were conducted over the temperature range of 30°–75°C. For thin disks (thickness 0.02 cm) of rigid PVC (0% plasticizer), no measurable

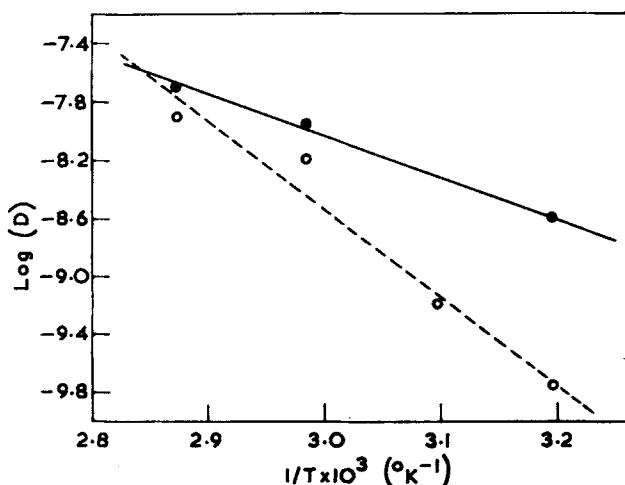


Fig. 2. Arrhenius plot of  $\log D$  vs  $1/T$  for diffusion in 20% plasticized PVC (O----) and 30% plasticized PVC (●——).

TABLE IV  
Values of Diffusion Coefficients for 2,4-Dihydroxybenzophenone in Various Polymers at 25°C

Polymer	$D$ , cm <sup>2</sup> /sec	Reference
Isotactic polypropylene	$5.4 \times 10^{-13}$	1
High-density polyethylene B	$3.2 \times 10^{-11}$	1
High-density polyethylene A	$5.4 \times 10^{-11}$	1
Low-density polyethylene	$4.6 \times 10^{-10}$	1
Polyurethane E.1	$1.6 \times 10^{-10}$	3
Polyurethane E.2	$2.7 \times 10^{-9}$	3
20% Plasticized PVC	$2.0 \times 10^{-11}$	This paper
30% Plasticized PVC	$8.6 \times 10^{-10}$	This paper
40% Plasticized PVC	$7.0 \times 10^{-9}$	This paper
50% Plasticized PVC	$1.5 \times 10^{-8}$	This paper

diffusion had occurred even after 700 hr at 75°C. In the case of the 10% plasticized PVC, no diffusion was detected below 50°C; but it was just detectable at higher temperatures after very long times: after 700 hr at 62°C and 400 hr at 75°C. So that when the temperature is below the  $T_g$  of the polymer (Table II), diffusion of the 2,4-dihydroxybenzophenone must be extremely slow and remains undetected by the present technique.

Diffusion coefficients were obtained for plasticizer concentrations of 20%, 30%, 40%, and 50%. At each plasticizer concentration, measurements were carried out for at least three temperatures. Typical results are shown in Figure 1 for the diffusion of the stabilizer in 30% plasticized PVC at 40°C. The open circles represent the experimental data, the solid curve being the theoretical curve corresponding to a value of  $2.54 \times 10^{-9}$  cm<sup>2</sup>/sec for the diffusion coefficient. The accuracy and reproducibility of the values of the diffusion coefficients were the same as in previous work.<sup>3</sup>

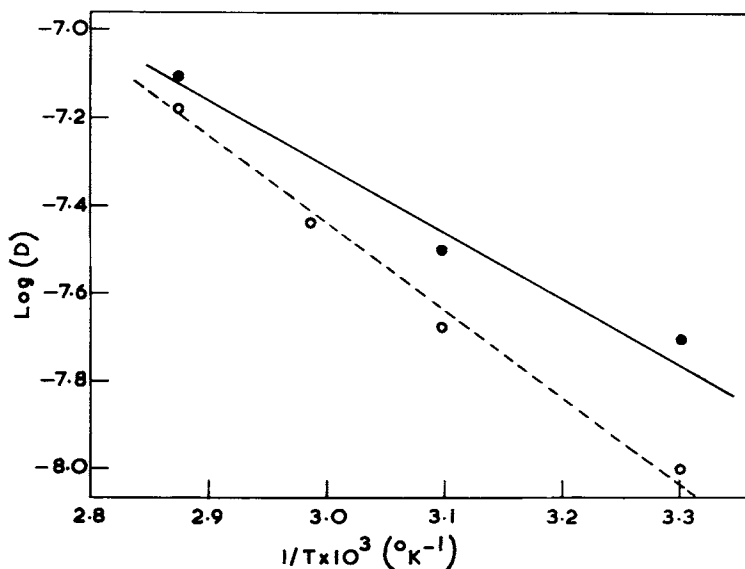


Fig. 3. Arrhenius plot of  $\log D$  vs  $1/T$  for diffusion in 40% plasticized PVC (O----) and 50% plasticized PVC (●—).

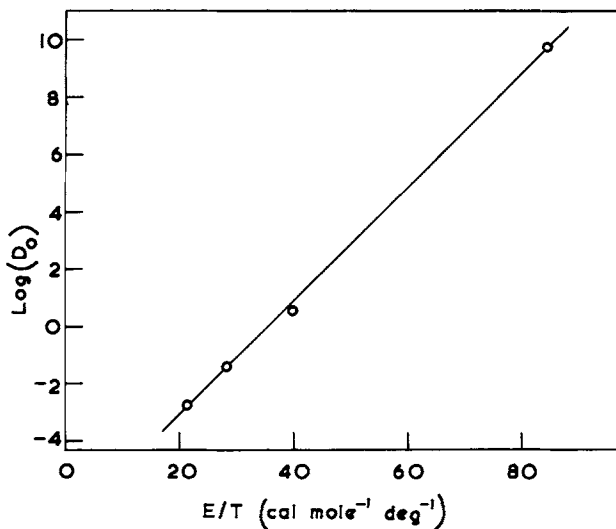


Fig. 4. Relationship between  $\log D_0$  and  $E/T$  for diffusion in plasticized PVC.

Plots of  $\log D$  versus  $1/T$ , for the various plasticizer concentrations are presented in Figures 2 and 3. The values of  $D_0$  and  $E$ , in the Arrhenius expression  $D = D_0 \exp(-E/RT)$ , obtained from these graphs are given in Table III.

As the plasticizer concentration increases, the polymer becomes more flexible ( $T_g$  decreases), which produces a decrease in the activation energy for diffusion. The decrease in the activation energy is accompanied by a decrease in the corresponding value of  $D_0$ , a phenomenon which has been noted previously for diffusion in a number of polymer systems.<sup>8-11</sup> Thus, the decrease in activation energy is compensated somewhat by a decrease in the entropy of activation as the polymer becomes more flexible.

An empirical linear relation between  $\log D_0$  and  $E/T$  has already been established for a number of systems,<sup>8-11</sup> and a similar situation exists in the present work as shown in Figure 4 ( $T$  is the mean value of the temperature range over which  $D_0$  and  $E$  were obtained). The correlation

$$\log D_0 = -7.1 + 0.20E/T$$

is obtained from this figure which, together with the Arrhenius expression  $D = D_0 \exp(-E/RT)$ , leads to the equation

$$\log D = -7.1 - 0.019E/T$$

This is similar to the corresponding equations for the diffusion of gases in rubbers<sup>8,9</sup> and for organic compounds in polyolefins.<sup>11</sup> A possible use of such an equation may be to estimate a value of the activation energy for diffusion from the measurement of  $D$  at one temperature only.

In Table IV, the diffusion coefficients that we have obtained for the diffusion of 2,4-dihydroxybenzophenone in various polymers at 25°C are listed; the values were calculated at this temperature from the appropriate Arrhenius equations. There is a very wide range of values for the diffusion coefficients in the different polymers ranging from  $5.4 \times 10^{-13}$  cm<sup>2</sup>/sec in isotactic polypropylene up to 1.5

$\times 10^{-8}$  cm<sup>2</sup>/sec in the 50% plasticized PVC. Correlations of the changes in the values of the diffusion coefficients with changes in the structure of the polymers have been pointed out previously<sup>1,3</sup> as well as in the present paper. The data in Table IV will be reliable for predicting the diffusion behavior of the stabilizer in the polymers at room temperature since the extrapolation of the results using the Arrhenius equation will be fairly accurate, 25°C being only just outside the experimental temperature range.

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