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THE EFFECT OF PRESSURE ON SOME FREE-RADICAL REACTIONS OF 1:2-DICHLORETHYLENE

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We have measured the effect of pressure on the rates of interconversion of *cis*- and *trans*-1:2-dichlorethylene catalyzed by iodine in the liquid phase. The values of the first-order rate constants for the *cis* isomer at 150° C were found to be $0.43 \times 10^{-4} \sqrt{[I_2]}$ sec⁻¹ at the vapour pressure of the solution, and $0.77 \times 10^{-4} \sqrt{[I_2]}$ sec⁻¹ at 3000 atm; the corresponding values for the *trans* isomer are $1.00 \times 10^{-4} \sqrt{[I_2]}$ sec⁻¹ and $2.23 \times 10^{-4} \sqrt{[I_2]}$ sec⁻¹ ($[I_2]$ in mole fraction). The acceleration by pressure can be attributed to the increased rate at which iodine atoms add to the double bonds. Some subsidiary experiments indicated that the equilibrium between the two isomers is displaced towards the more dense *cis* form at high pressures.

In the presence of benzoyl peroxide, 1:2-dichlorethylene undergoes both isomerization and polymerization. We have found that the polymerization is accelerated by an increase in pressure, whereas the isomerization is retarded. A possible mechanism of these reactions is discussed.

The effect of pressure on free-radical reactions involving ethylenic double bonds is of interest because of its bearing on the mechanism of polymerizations at high pressures. A simple reaction of this kind is the *cis-trans* isomerization of 1:2-dichloroethylene catalyzed by iodine. Wood and Dickinson¹ have investigated the kinetics of the rearrangement at low pressures and found that the rate is proportional to the square root of the iodine concentration: they concluded that iodine atoms are the effective catalysts. In the present work we have measured both the rate of the isomerization and the approximate equilibrium concentrations of the isomers, at pressures up to 3000 atm.

We have also examined the effect of pressure on the transformations of 1:2-dichlorethylene in the presence of benzoyl peroxide, which induces both isomerization and polymerization. Weale² had previously investigated the polymerization at pressures up to 8000 atm, and concluded that the yield and molecular weight of the product increase with the pressure. Our experiments confirm this, and also establish the existence of a definite pressure effect on the rate of isomerization.

EXPERIMENTAL

MATERIALS.—The pure *cis* and *trans* isomers of 1:2-dichlorethylene were obtained from the commercial solvent by three-fold distillation in a 5-ft. glass distillation column packed with Fenske helices. The physical properties of the final fractions are compared with published values in table 1.

TABLE 1.—PROPERTIES OF *cis*- AND *trans*-1:2-DICHLORETHYLENE

	Timmermans ³		found	
	<i>cis</i>	<i>trans</i>	<i>cis</i>	<i>trans</i>
boiling point/°C	60.5	47.7	60.50	47.85
dielectric constant at 25° C	9.31	2.145	9.262	2.164
molar volume/cm ³ at 20° C	75.62	77.25		

Benzoyl peroxide was purified by the method of Augood, Hey and Williams.⁴ The iodine was of resublimed analytical quality.

PROCEDURE.—The low-pressure reactions were carried out in test-tubes which had been swept out with CO₂ and then sealed. The pressure during reaction was thus slightly greater than the vapour pressure of the solution.

The high-pressure reactions were carried out in 10 ml cylindrical glass cells which were ground internally and had well-fitting glass plugs which could slide into the cells and transmit the pressure to the reaction mixture. The cells were immersed in oil in a steel bomb connected to a pumping system which delivered oil at pressures up to 3000 atm. The bomb could be immersed in an oil thermostat. Since the temperature of the reactions was above the boiling point of dichlorethylene it was necessary to raise the pressure in the bomb before immersing it in the hot oil bath, and to cool the bomb again before releasing the pressure. These operations were strictly standardized to reduce the uncertainty in the timing of the reaction.

IODINE REACTIONS.—Solutions of iodine in each isomer were made up by weighing. After the reaction, the iodine was removed by immersing a spiral of freshly cleaned copper wire in the solution; in the low-pressure reactions this left a colourless liquid but the 3000 atm mixtures often remained brown, however long the copper wire was left in them. These solutions became clear on heating and precipitated a very small amount of a brown solid containing iodine. The dielectric constant of the solution was found not to be affected by the presence of this material. Distillation of the reaction product showed that no dimer or higher polymers were formed.

The reaction mixture was analysed for the *cis* and *trans* isomers by measuring its dielectric constant in the Henriquez type of apparatus described by David, Hamann, and Pearse.⁵ Measurements were made on two 3-ml samples of each mixture, in a capacity cell which had been calibrated with highly purified benzene assuming this to have a dielectric constant of 2.2725 at 25° C. The concentration of the isomers was found by comparing the measured dielectric constant with the values determined by Ketelaar, van Velden, Broers, and Gersmann⁶ for synthetic mixtures of the isomers, a correction being made for the small difference between their values for the pure components and ours.

In the rate measurements, the reactions were run at 150° C and were taken to only low degrees of conversion in order to avoid the complicating effect of the reverse reaction. Some reactions were also run at 185° C, to high degrees of conversion, in an attempt to estimate the equilibrium constant for the isomerization.

BENZOYL PEROXIDE REACTIONS.—Only the *cis* isomer was used in these reactions. The procedure was the same as for the iodine isomerizations except in the method of analysis. Here the total reaction product was weighed and then distilled to separate the monomer from the polymer. The dielectric constant of the fraction boiling below 61° C was measured to find the extent of isomerization in the monomer, and the residue was weighed to determine the yield of polymer.

The high-boiling fractions from several runs were combined and distilled at reduced pressure. They gave a main fraction boiling between 102° and 107° C at 35 mm Hg, as well as a small amount of high boiling polymer. The main fraction had a refractive index $n_D^{25} = 1.514$ and probably consisted of the dimer 1:3:4:4-tetrachlorobutene-1, which Weale² found to boil between 95° and 100° C at 30 mm Hg and to have $n_D^{20} = 1.517$.

RESULTS

IODINE REACTIONS.—Wood and Dickinson¹ found that the first-order rate constant for the isomerization at low pressures is proportional to the square root of the iodine concentration and we have confirmed that this relation holds at high pressures. Fig. 1 illustrates the course of the isomerizations at 150° C, and table 2 lists the rate constants calculated from the slopes of the lines in fig. 1.

The results of the measurements at 185° C are given in table 3, where the final column lists the ratio of the amount of *trans* (*T*) to *cis* (*C*) isomer at the end of the reaction. An extrapolation of the results indicates that the equilibrium values of this ratio would be about 0.48 at the vapour pressure of the mixture and 0.41 at 3000 atm.

BENZOYL PEROXIDE REACTIONS.—Table 4 gives our results for the reactions in the presence of benzoyl peroxide. The fifth column lists the amount of polymer as a weight percentage of the total mixture, and the sixth column gives the extent of isomerization in the remaining monomer: the final column lists the ratio of these two quantities.