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REACTIONS OF 1 : 2-DICHLORETHYLENE

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

BY A. H. EWALD, S. D. HAMANN AND J. E. STUTCHBURY

C.S.I.R.O. Division of Industrial Chemistry, High Pressure Laboratory,
University of Sydney, Australia

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 Dickinson [1] 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. Weale [2] 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	
	cis	*trans*	*cis*	*trans*
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/cm³ at 20° C	75·62	77·25		

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

PROCEDURE.—The low-pressure reactions were carried out in test-tubes which had been swept out with CO_2 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 re-actions 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 un-certainty 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 di-electric 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 di-electric 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 Gersmann [6] 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 meas-ured 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 Weale [2] 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 Dickinson [1] 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.

TABLE 2.—FIRST-ORDER RATE CONSTANTS FOR THE ISOMERIZATION OF
1 : 2-DICHLORETHYLENE CATALYZED BY IODINE AT 150° C

Concentration of iodine $[I_2] \approx 0.5$ mole %

P/atm	$cis \rightarrow trans$		$trans \rightarrow cis$	
a*	$k_C = 0.43 \times 10^{-4}\sqrt{[I_2]}$ sec^{-1}		$k_T = 1.00 \times 10^{-4}\sqrt{[I_2]}$ sec^{-1}	
1500	0.57	,, ,,	1.67	,, ,,
3000	0.77	,, ,,	2.23	,, ,,

* a is the vapour pressure of the solution (≈ 10 atm).

TABLE 3.—THE ISOMERIZATION OF cis-1 : 2-DICHLORETHYLENE CATALYSED
BY IODINE AT 185° C

P/atm	$[I_2]$/mole %	time/h	% conversion	$[T]/[C]$
a*	0.812	3.1	28.4	0.397
a	0.390	3.2	25.2	0.337
a	0.261	6	29.3	0.415
a	0.390	6	30.8	0.436
a	0.390	8	31.4	0.458
a	0.812	9.5	32.0	0.471
3000	0.416	2.8	27.0	0.370
3000	0.416	3.1	27.5	0.380
3000	0.390	8	27.2	0.374
3000	0.416	9.5	28.8	0.404

* a is the vapour pressure of the solution (≈ 20 atm).

TABLE 4.—THE REACTIONS OF cis-1 : 2-DICHLORETHYLENE IN THE PRESENCE OF
BENZOYL PEROXIDE

P/atm	temp./° C	initial conc. benzoyl peroxide (mole %)	time/min	polym. (wt. %)	isom. [(mole %)	polym./isom.
a*	81	0.072	150	7.5	0.80	9.4
a	81	0.392	150	14.4	1.95	7.4
a	81	0.392	240	16.9	2.80	6.0
3000	81	0.392	150	26.8	0.75	35.8
3000	81	0.392	240	33.0	1.10	30.0
a	90.5	0.405	70	15.0	3.1	4.8
a	90.5	0.405	120	21.0	5.2	4.0
3000	90.5	0.398	120	40.0	1.60	25.0
a	120	0.405	120	20.1	10.0	2.0
3000	120	0.405	120	36.8	11.7	3.1
a	135	0.405	65	17.0	10.7	1.6
a	135	0.405	120	19.0	11.4	1.7
3000	135	0.405	120	33.4	11.2	3.0
a	150	0.077	90	8.4	7.9	1.1
a	150	0.309	90	13.9	10.6	1.3
a	150	0.309	303	15.4	12.0	1.3

* a is the vapour pressure of the mixture (2-10 atm).

From the trend of the results, particularly the yield of polymer, it appears that at temperatures above 90·5° C the extent of reaction was limited by the amount of benzoyl peroxide initially present and this suggests that the peroxide is consumed in some step of the process. Fig. 2 shows the effect of pressure on the reactions at 81° C.
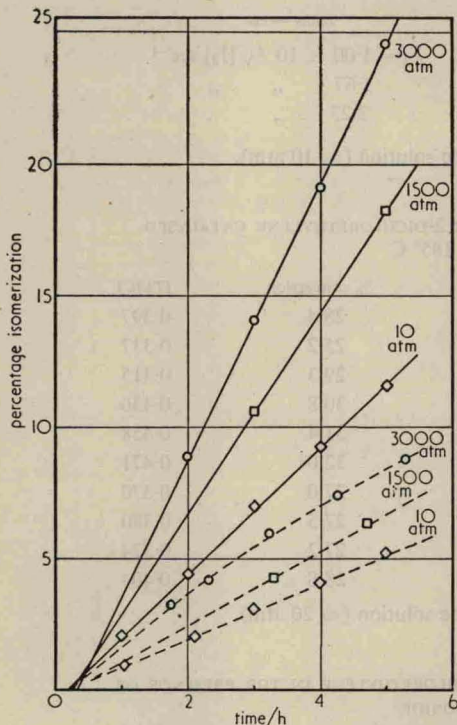

FIG. 1.—The isomerization of 1 : 2-dichlorethylene catalyzed by 0·5 mole % of I_2 at 150° C. Solid curves: *trans → cis*; dashed curves: *cis → trans* isomerization.
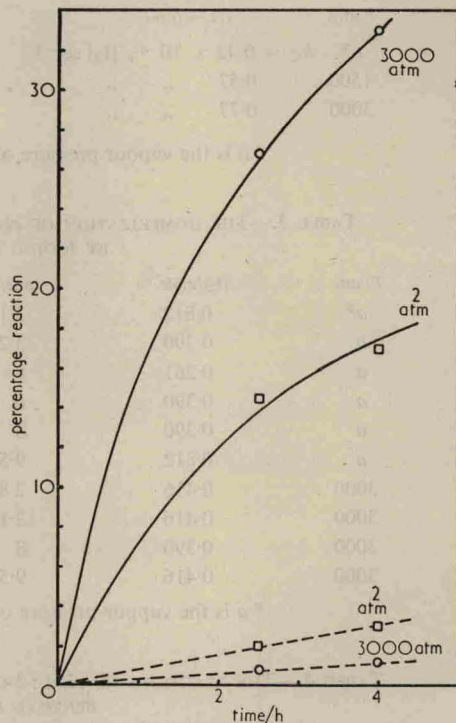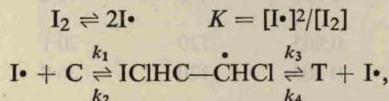
FIG. 2.—The reactions of *cis*-1 : 2-dichlorethylene in the presence of 0·392 mole % benzoyl peroxide at 81° C.
Solid curves: wt. % polymer formed; dashed curves: mole % isomerization.

DISCUSSION

IODINE REACTIONS

It is very likely that the isomerization proceeds according to the following scheme:

$$I_2 \rightleftharpoons 2I\bullet \qquad K = [I\bullet]^2/[I_2]$$

$$I\bullet + C \underset{k_2}{\overset{k_1}{\rightleftharpoons}} ICIHC—\overset{\bullet}{C}HCl \underset{k_4}{\overset{k_3}{\rightleftharpoons}} T + I\bullet,$$

where C and T denote the *cis* and *trans* isomers. It can be assumed that the time required for internal rotation in the addition complex is small compared with its lifetime.

Starting with the pure *cis* isomer the reverse reaction 4 can be ignored in the early stages, and if we assume a steady-state concentration of addition complexes we can derive the first-order rate constant for the conversion in the form:

$$k_C = \frac{k_1 (K_C [I_2])^{\frac{1}{2}}}{1 + k_2/k_3}.$$

Similarly for a reaction starting with the *trans* isomer:

$$k_T = \frac{k_4 \, (K_T \, [I_2])^{\frac{1}{2}}}{1 + k_3/k_2}.$$

The subscripts C and T indicate that the quantities relate to rates and equilibria in the pure *cis* and *trans* isomers. For a particular concentration of iodine the ratio k_C/k_T is

$$\frac{k_C}{k_T} = \frac{k_3 k_1}{k_2 k_4} \left(\frac{K_C}{K_T}\right)^{\frac{1}{2}}.$$

It should be noted that this is *not* equal to the equilibrium constant for the isomerization ($k_3 k_1/k_2 k_4$) because the values of K for the dissociation of iodine are unlikely to be the same in the two isomers.

The above scheme accounts for the observed proportionality between the rates of isomerization and the square root of the iodine concentration. The same dependence would hold if iodine ions, rather than iodine atoms were the active catalysts, but the rate should then be strongly affected by a change in the dielectric constant of the medium, whereas the experiments of Wood and Dickinson [1] have shown that it is not.

Our measurements (table 2) establish that both k_C and k_T are increased by pressure. These changes could hardly be caused by an alteration in the ratio k_2/k_3 since this would affect the forward and reverse reactions in the opposite sense (see formulae above). They could, however, be due to increases in K_C and K_T or in k_1 and k_4. Unfortunately there is no direct information on the effect of pressure on the dissociation of iodine molecules into atoms in solution, but it has been found [7] that the analogous dissociation of N_2O_4 into NO_2 radicals in solution is suppressed by an increase in pressure. We should expect the iodine equilibrium to be similarly affected, so that K_C and K_T would be reduced at high pressures. It follows that the observed accelerations arise from increases in the bimolecular rate constants k_1 and k_4 which relate to the addition of iodine atoms to the double bonds. This indicates that the partial formation of a C—I bond in the transition state is accompanied by a contraction of the system.
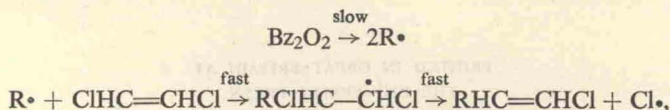
Turning to the equilibrium between the two isomers, we note that the molar volume of the *trans* form is greater by 1·63 cm^3 than that of the *cis* form at 20° C and 1 atm (table 1). If this difference ΔV were independent of the temperature and pressure, then the relation
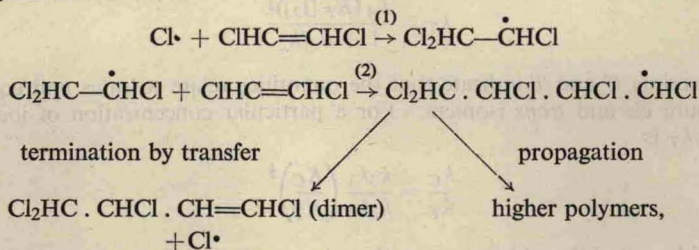
$$\partial \ln K/\partial P = -\Delta V/RT$$

would require the equilibrium constant, $K = [T]/[C]$, to decrease by 12 % between 1 atm and 3000 atm at 185° C. Our experimental results indicate that it decreases by about 14 %.

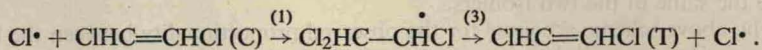### BENZOYL PEROXIDE REACTIONS.

In the presence of benzoyl peroxide, 1 : 2-dichlorethylene undergoes both isomerization and polymerization. It is known that in other polymerizations initiated by benzoyl peroxide the rate-determining step in the initiation is the slow decomposition of the peroxide into radicals R•; the subsequent addition of these radicals to double bonds being very fast. On this basis we suggest that the initiating steps are:

$$\text{Bz}_2\text{O}_2 \xrightarrow{\text{slow}} 2\text{R}\bullet$$

$$\text{R}\bullet + \text{ClHC}{=}\text{CHCl} \xrightarrow{\text{fast}} \text{RClHC}{\overset{\bullet}{-}}\text{CHCl} \xrightarrow{\text{fast}} \text{RHC}{=}\text{CHCl} + \text{Cl}\bullet,$$

and following Schmerling and West [8] we can assume that the subsequent steps in the polymerization are:

$$Cl\cdot + ClHC{=}CHCl \xrightarrow{(1)} Cl_2HC{-}\overset{\cdot}{C}HCl$$

$$Cl_2HC{-}\overset{\cdot}{C}HCl + ClHC{=}CHCl \xrightarrow{(2)} Cl_2HC \cdot CHCl \cdot CHCl \cdot \overset{\cdot}{C}HCl$$

termination by transfer   propagation

$Cl_2HC \cdot CHCl \cdot CH{=}CHCl$ (dimer)   higher polymers,
$+ Cl\cdot$

whereas the isomerization probably occurs by the mechanism:

$$Cl\cdot + ClHC{=}CHCl\ (C) \xrightarrow{(1)} Cl_2HC{-}\overset{\cdot}{C}HCl \xrightarrow{(3)} ClHC{=}CHCl\ (T) + Cl\cdot\ .$$

This scheme explains the peculiar structure of the dimer, and the fact that benzoyl peroxide is consumed in the reaction. It is unlikely that the small amount of $RHC{=}CHCl$ could have been isolated in our analyses.

It will be seen that the addition complex $Cl_2HC{-}\overset{\cdot}{C}HCl$ can either dissociate into the *trans* isomer by reaction (3) or add to a monomer molecule by reaction (2). The dissociation would involve an extension of the C—Cl bond while the addition would lead to a contraction of the $\overset{\cdot}{C} \ldots C$ distance, so that we might expect reaction (3) to be retarded by pressure and reaction (2) to be accelerated. In agreement with this, our results (fig. 2) show that the overall rates of isomerization and polymerization are respectively decreased and increased by a rise in pressure. But of course, these overall rates also depend on the steady-state concentration of addition complexes, and there is no easy way of estimating how that varies with the pressure.

[1] Wood and Dickinson, *J. Amer. Chem. Soc.*, 1939, **61**, 3259.
[2] Weale, *J. Chem. Soc.*, 1952, 2223.
[3] Timmermans, *Physico-Chemical Constants of Pure Organic Compounds* (Elsevier, 1950).
[4] Augood, Hey and Williams, *J. Chem. Soc.*, 1952, 2100.
[5] David, Hamann and Pearse, *J. Chem. Physics*, 1951, **19**, 1491.
[6] Ketelaar, van Velden, Broers and Gersmann, *J. Physic. Chem.*, 1951, **55**, 987.
[7] Ewald, *Faraday Soc. Discussions*, 1956, **22**.
[8] Schmerling and West, *J. Amer. Chem. Soc.*, 1949, **71**, 2015.