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.
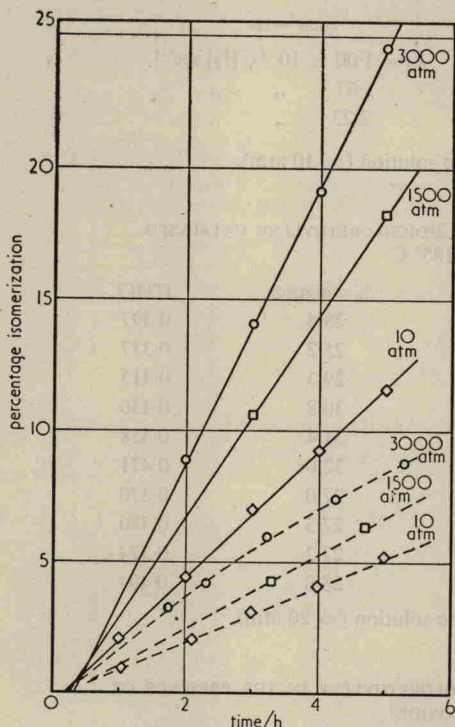

FIG. 1.—The isomerization of 1 : 2-dichloroethylene catalyzed by 0·5 mole % of I_2 at 150° C. Solid curves: trans → cis; dashed curves: cis → trans isomerization.
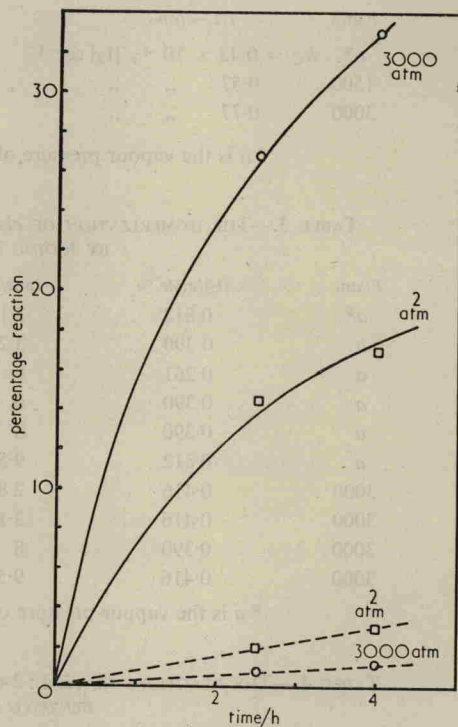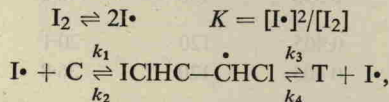
FIG. 2.—The reactions of cis-1 : 2-dichloroethylene in the presence of 0·392 mole % benzoyl peroxide at 81° C. Solid curves: wt. % polymer formed; dashed curves: mole % isomerization.

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 :

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