

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

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

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

\*  $a$  is the vapour pressure of the solution ( $\approx 10$  atm).TABLE 3.—THE ISOMERIZATION OF  $cis$ -1:2-DICHLOROETHYLENE CATALYSED BY IODINE AT 185° C

$P/\text{atm}$	$[I_2]/\text{mole } \%$	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 ( $\approx 20$  atm).TABLE 4.—THE REACTIONS OF  $cis$ -1:2-DICHLOROETHYLENE IN THE PRESENCE OF BENZOYL PEROXIDE

$P/\text{atm}$	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.

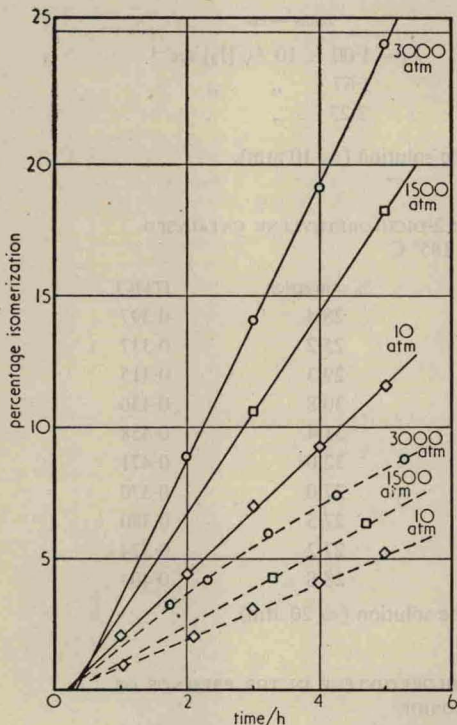


FIG. 1.—The isomerization of 1:2-dichloroethylene catalyzed by 0.5 mole % of  $I_2$  at 150° C. Solid curves: *trans* → *cis*; dashed curves: *cis* → *trans* isomerization.

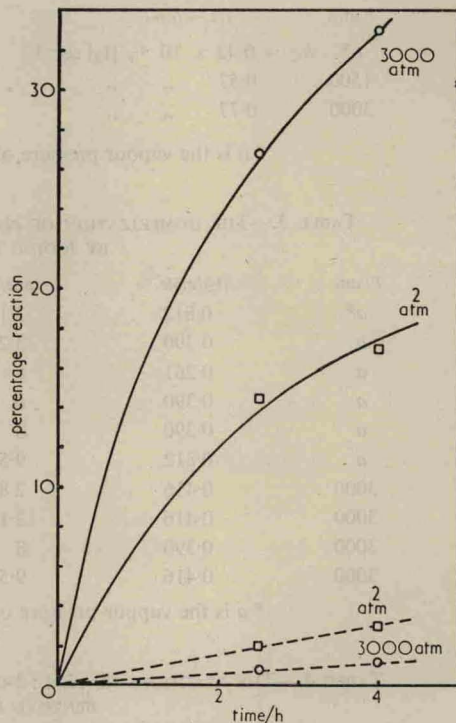


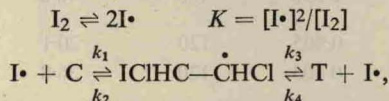
FIG. 2.—The reactions of *cis*-1:2-dichloroethylene in the presence of 0.392 mole % benzoyl peroxide at 81° C.

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:



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:

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