

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 Dickinson¹ 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 found⁷ 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.

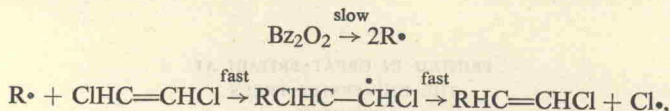
Turning to the equilibrium between the two isomers, we note that the molar volume of the *trans* form is greater by 1.63 cm³ than that of the *cis* form at 20° C and 1 atm (table 1). If this difference ΔV were independent of the temperature and pressure, then the relation

$$\partial \ln K / \partial P = -\Delta V / RT$$

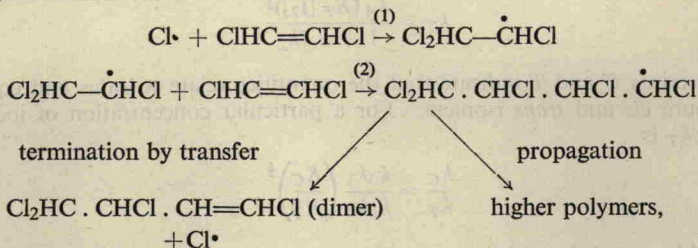
would require the equilibrium constant, $K = [T]/[C]$, to decrease by 12 % between 1 atm and 3000 atm at 185° C. Our experimental results indicate that it decreases by about 14 %.

BENZOYL PEROXIDE REACTIONS.

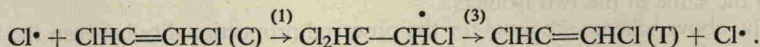
In the presence of benzoyl peroxide, 1:2-dichlorethylene undergoes both isomerization and polymerization. It is known that in other polymerizations initiated by benzoyl peroxide the rate-determining step in the initiation is the slow decomposition of the peroxide into radicals $R\cdot$; the subsequent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



and following Schmerling and West⁸ we can assume that the subsequent steps in the polymerization are:



whereas the isomerization probably occurs by the mechanism:



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 $\text{RHC}=\text{CHCl}$ could have been isolated in our analyses.

It will be seen that the addition complex $\text{Cl}_2\text{HC}-\dot{\text{C}}\text{HCl}$ 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 $\dot{\text{C}}\dots\text{C}$ 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.

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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 Pearce, *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.