Reaction of the Chloroallyl Radical with Molecular Chlorine

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The relative reactivities of the two sites of the chloroallyl radical towards a chlorine molecule have been measured at 350—500 °C; the ratio of rate constants for the formation of 1,3- and 3,3-dichloropropene is given by:

$$k_{1,3}/k_{3,3} = 10^{0.73 \pm 0.10} \exp{(+1130 \pm 300/RT)}$$

CHLORINATION of propene at temperatures above 350 °C leads principally to the formation of allyl chloride by direct substitution of an allylic H atom.[1,2] A concurrent addition which occurs yields 1,2-dichloropropane; this is kept to a minimum by the use of low concentrations of chlorine and high temperatures.[3] Subsequent formation of 3,3-dichloropropene (3,3-DCP) and 1,3-dichloropropene (1,3-DCP) has been explained [2] in terms of the presence of mesomeric forms of the chloroallyl radical resulting from the abstraction of a second allylic H atom [equations (1)—(3)].

$$CH_2{=}CH{-}CH_2Cl + Cl \xrightarrow{k_2} CH_2\dot{=}CH\dot{=}CHCl + HCl \quad (1)$$

$$CH_2\dot{=}CH\dot{=}CHCl + Cl_2 \xrightarrow{k_3} CH_2Cl{-}CH{=}CHCl + Cl \quad (2)$$

$$\xrightarrow{k_3{}^*} CH_2{=}CH{-}CHCl_2 + Cl \quad (3)$$

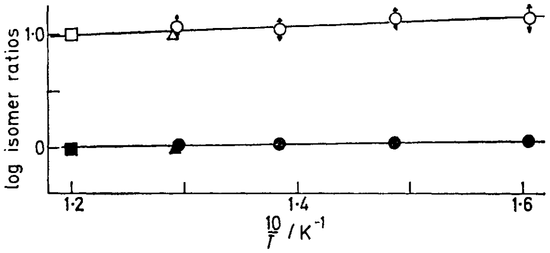
That similar distributions of the dichloropropenes are produced, both from allyl chloride and from the monochloropropenes, provides strong support for this mechanism.[2]

We have now measured the distribution of the isomeric dichloropropenes produced during the chlorination of propene over the temperature range 350—500 °C in a flow system. The reactor was a pyrolytic carbon-covered quartz tube at atmospheric pressure with 0·4—2·0 s residence times; the reaction products were measured by g.l.c. In all cases, the use of small $Cl_2 : C_3H_6$ ratios in the range 0·3 : 10 to 3 : 10 ensured that the formation of polychloro-compounds and addition products was slight. The main by-products were 1,2-dichloropropane at the highest chlorine concentrations and 2-chloropropene, chlorination of which leads to the formation of negligible amounts of 2,3-dichloropropene. It was verified that the isomer distribution of the dichloropropenes is independent of the chlorine concentration, of the presence of 1,2-dichloropropane, and of the amount of allyl chloride conversion, as expected from the mechanism of equations (1)—(3).

The experimental results obtained from the mean of series of 6—16 runs are given in the Table.

Distribution of dichloropropenes during allyl chloride chlorination *

Temp. (°C)	Dichloropropenes (mol %) 3,3-DCP	*cis*-1,3-DCP	*trans*-1,3-DCP	Total 1,3-DCP
350	7 ± 2	50 ± 1	43 ± 1	93 ± 2
400	7 ± 1	49 ± 1	44 ± 1	93 ± 1
450	8 ± 1·5	48 ± 1	44 ± 1	92 ± 1·5
500	8 ± 0·5	47 ± 0·5	45 ± 1	92 ± 0·5



Substitutive chlorination of allyl chloride: temperature dependence of the dichloropropene isomer ratios. 1.3-DCP/3,3-DCP: ○ this work; △ ref. 2; □ chlorination of a mixture of 1-monochloropropene isomers, ref. 2. *cis*-1,3-DCP/*trans*-1,3-DCP: ● this work; ▲ ref. 2; ■ chlorination of 1-monochloropropene mixed isomers, ref. 2

The present results, given as Arrhenius plots in the Figure where they are compared with literature data, yield the following values

$$[1,3\text{-DCP}]/[3,3\text{-DCP}] = 10^{0.73 \pm 0.10} \exp{(+1130 \pm 300/RT)} \quad (4)$$

$$[cis\text{-}1,3\text{-DCP}]/[trans\text{-}1,3\text{-DCP}] = 10^{-0.17 \pm 0.10} \exp{(+ 665 \pm 300RT)} \quad (5)$$

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[2] G. W. Hearne, T. W. Evans, H. L. Yale, and M. C. Hoff, *J. Amer. Chem. Soc.*, 1953, **75**, 1392.

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Throughout the paper activation energies are given in cal/mol.

From data on similar cases it is expected that the *cis* : *trans* ratio, which is independent of the extent of reaction, reaches its equilibrium value.[4] Comparison of the present results with the corresponding values for the 1,2-dichloroethylenes and the 1-monochloropropenes [respectively $10^{-0.02}$ exp $(+570RT)$ and $10^{0.04}$ (exp $(+706/RT)$ [4]] shows that the enthalpy term is practically constant within the limits of experimental error while the entropy term increasingly favours the *trans*-isomer on passing from a methyl substituent on the C-2 atom to a chlorine atom and to a chloromethyl radical.

Equation (4) shows that the attack of the chlorine molecule on the unchlorinated side of the chloroallyl radical is always favoured on enthalpy as well as entropy grounds. From the principle of least motion [5] it is expected that 'the difference in molecular structure (atomic position and electronic configuration) between reactants and products is smaller for the more rapidly formed product than for the less rapidly formed product' even when the reactant is a resonance-stabilized species. This suggests that the canonic form (I) is closer to the

$$\underset{\text{(I)}}{\cdot CH_2{-}CH{=}CHCl} \longleftrightarrow \underset{\text{(II)}}{CH_2{=}CH{-}\dot{C}HCl}$$

actual structure of the chloroallyl radical than (II) even though it is generally considered that the presence of a chlorine atom will stabilize a form such as (II).

Regardless of the fate of the unpaired electron, the predominance of (I) can be explained by the stabilization of the C=C π-bond by the p orbitals of the halogen as compared to the situation in (II).[6] Further, the presence of the electronegative $-CHCl$ group α to the double bond in (II) [compared to $-CH_2$ in (I)] is expected to destabilize the double bond. In other words, the relative stabilities of forms (I) and (II) do not depend on stabilization by the unpaired electron and its orbital which are the same for both systems.

Similar arguments can be used to show, in the absence of relevant thermochemical data, that 1,3-DCP resulting from the chlorination of (I) is more stable than 3,3-DCP. For these products, a comparison with the methylated compounds (respectively pent-2-ene and 3-methylbut-1-ene, shows that the 1,3-compound has a higher entropy (by *ca.* 2—3 units) than the 3,3-compound depending on the choice of the *trans*- or *cis*-isomer) which is comparable to the 3·3 e.u. difference found from equation (4).

This provides an alternative interpretation of our results. Since both transition states are similar to the resulting products the relative stabilities of the latter reflect those of the transition states; *i.e.* the thermodynamically favoured reaction is also the faster. From this, one could expect that the transition state leading to 1,3-dichloropropene is lower in free energy than that leading to 3,3-dichloropropene in agreement with our experimental results.

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