Unexpected Selectivity in the Chlorination of the Halogenocycloalkanes

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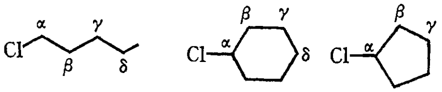
WE have previously shown that even the most electronegative substituent in a linear alkane has little or no effect on the rate of chlorine atom atom attack beyond the β-position, when the reaction is carried out in the gas phase.[1] The situation for chlorination in solution was very different and a substituent can show an effect, at least, as far as the ϵ-position. Russell and his co-workers[2,3] have chlorinated chlorocyclohexane and chlorocyclopentane in solution and have obtained results which fitted well with the previous ideas about polar influences in these reactions. In particular they observed rates of attack in the order $\alpha < \beta < \gamma < \delta$. We have now studied the chlorination of these compounds in the gas phase and have obtained a selectivity pattern quite different to the solution phase work and to our own previous work on linear alkanes.

The relative rates of attack at the α-positions are fairly similar; there is greater uncertainty in the values between different molecules than for different sites in the same molecule. The striking feature of these results is that the β-position is more reactive than the γ-position in both cyclic molecules, the difference for chlorocyclopentane being very marked. Russell found the rate of chlorination at the β-position in bromocyclopentane abnormally high and attributed this to bridging by the bromine atom. Such a hypothesis,

Chlorination in the gas phase at 70°

RS$^{x}_{1°}$ (1° ≡ the primary hydrogen atoms in n-butane)



	α	β	γ	δ
1-Chloropentane	0·8	2·1	3·7	(3·7)
Chlorocyclohexane	1·4	4·7	4·4	6·2
Chlorocyclopentane	1·0	6·0	4·7	—

(RS$^{x}_{1°}$ values are calculated from the sum of the *cis*- and *trans*-isomers at the β, γ, and δ positions.)

results appear to represent a major setback for the though reasonable for bromine atoms, at low temperatures in the liquid phase, seems unlikely for chlorine atoms in the gas phase and at high temperatures (the β-position is still chlorinated more rapidly than the γ-position for both cyclic molecules at temperatures around 200°). These simple polar theories.[4,5] Further work is in progress in order to obtain data for all isomers (*cis* and *trans*) over a wide range of temperatures.

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