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REACTIVITIES OF C_{SEC}- H BONDS TOWARDS CHLORINE IN ALKANES AND ALKANE CARBOCHLORIDES[1]

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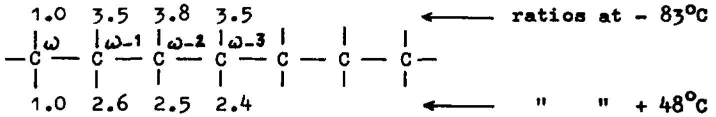
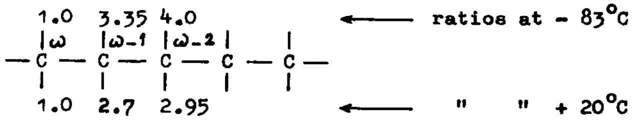
Some alkanes (pentane, hexane and heptane) and alkane carbochlorides (propionyl, butyryl, valeryl, caproyl and octanoyl chloride) were chlorinated under irradiation ($\lambda > 310$ nm) in the liquid phase at various temperatures without and in the presence of benzene and carbon disulphide as a solvent[2]. Chlorine was dissolved in the substrate in darkness (molar ratio = 1 : 10), whereupon the mixture was irradiated. Di- and higher chlorinated products being almost absent, ratios of monochloro compounds give information on relative reactivities of C-H bonds.

Subsequent conclusions can be drawn on the behaviour of alkanes:

1. C_{sec}- H bonds always have higher reactivities than C_{pr}- H bonds. The ratio of rate constants at $C_{\omega-2}$ and C_{ω} in heptane at 48°C amounts to 2.4, that at -70°C in CS_2 (molar ratio of C_7H_{16}: CS_2 = 1 : 32) to 52.
2. Increase of reactivity with temperature is higher at $C_{\omega-1}$ than at $C_{\omega-2}$

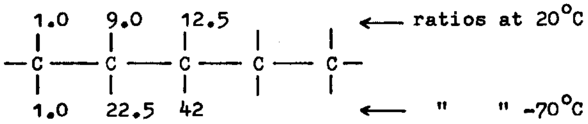


Reactivity at $C_{\omega-2}$ surpasses that at $C_{\omega-1}$ below -17°C. Thus, at higher temperature substitution at $C_{\omega-1}$ is faster. In hexane the $C_{\omega-1}$- H bond is more reactive than the $C_{\omega-2}$- H bond above -3°C; in pentane this alternation does not occur below the boiling point (36°C).



3. The ratio of substitution rates at C_{sec} and C_{pr} decreases with rising temperature, especially the relative rate at $C_{\omega-2}$ (Cf. section 2).

4. In complexing solvents reaction rates are lower, but higher amounts of secondary chloro products are formed[3].

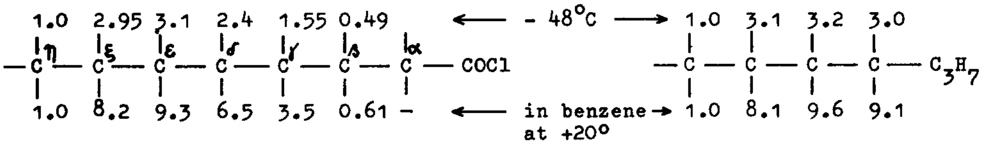


$C_5H_{12} : CS_2 = 1 : 4$

Bond $\underset{\omega-1}{C-H}$ is the most reactive one at all temperatures in pentane again.

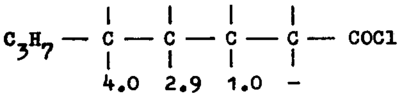
As for the photochlorination of alkane carbochlorides the following rules apply.

5. In octanoyl chloride the apolar end of the molecule behaves analogously to the corresponding fragment of heptane. Here ratios of rates observed in chlorinations at -48°C and in benzene (substrate : solvent = 1 : 4) at +20°C are given.

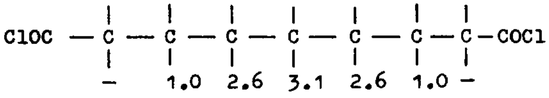


Again below -17°C and in solvents at all temperatures the ω-2(= ε)-position is the most reactive one.

6. The hydrogen atoms up to and including those at the δ-position in octanoyl chloride are strongly deactivated by the carbochloride group, those at the ε-position only weakly. Compare the reactivities at C_ζ, C_ε and C_δ in octanoyl chloride with those at $C_{\omega-1}$, $C_{\omega-2}$ and $C_{\omega-3}$ in heptane and also rate ratios in chlorinations at 20° of octanoyl and azelayl chloride at C_β, C_γ and C_δ.



octanoyl chloride



azelayl chloride

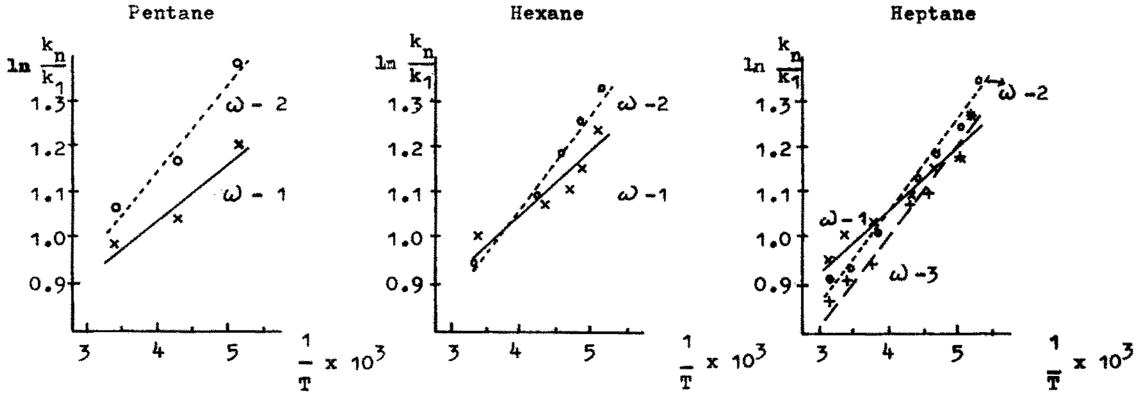
7. More than the chlorinations of higher alkane carbochlorides studied, reactions of propionyl chloride give information on the effect of the carbochloride group on reactivities of adjacent C-H bonds. Subsequent chlorinations are compared.

Cl - C = O	-70°C	+20°C	-70°C in CS_2 substr.:solv.=1 : 4	+20° in CS_2 substr.:solv.=1 : 4
$-C^{\alpha}-$	0.20	0.36	1.55	0.75
$-C^{\beta}-$	1.0	1.0	1.0	1.0

Due to the deactivation by the COCl-group the C^{α}_{sec}- H bond is less reactive than the C^{β}_{prim}-H bond in 3 experiments. It is remarkable that the solvent enhances the rate at Cα especially at low temperature: at -70° the C_{sec}- H bond is the more reactive one again.

Explanation of results.

All chlorinations described are assumed to be radical processes in which the rate of hydrogen abstraction determines the formation of the monochloro substitution products. From the relation between logarithms of rate ratios (ln k_n/k_ω) and 1/T, differences of activation energies of abstractions of hydrogen from C_ω and C_n ($E_\omega - E_n$) and the ratios of frequency factors (A_n/A_ω) are calculated. In photochlorinations in the absence of a solvent there will be only little breaking of the C-H bond in the transition-state of the abstraction by a chlorine atom. Chlorine atoms predominantly attack C-H bonds with the highest electron availability while the strength of the C-H bond is not very important. For the photochlorinations of the alkanes the following data were obtained.

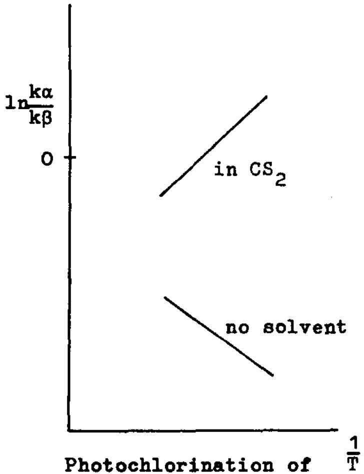


$E_\omega - E_{\omega-1}$:	0.23 kcal/mole	0.27 kcal/mole	0.27 kcal/mole
$A_{\omega-1}/A_\omega$:	1.7	1.7	1.7
$E_\omega - E_{\omega-2}$:	0.37 "	0.39 "	0.40 "
$A_{\omega-2}/A_\omega$:	1.5	1.3	1.3
$E_\omega - E_{\omega-3}$:	---	---	0.38 "
$A_{\omega-3}/A_\omega$:	---	---	1.3

The activation energies being lower at $C_{\omega-2}$ than at $C_{\omega-1}$, abstraction of hydrogen from $C_{\omega-2}$ is the fastest reaction at low temperature. The shift of maximum reactivity from $C_{\omega-2}$ to $C_{\omega-1}$ by elevating the temperature, can be ascribed to differences in frequency factors.

Chlorinations carried out in a solvent complexing the chlorine atom can be explained by assuming that hydrogen abstraction here involves a transition state with more bond breaking. Thus, the difference of activation energies of abstraction from C_{prim} and C_{sec} in alkanes and from C_{prim} and C_{sec} ($\omega-1$ — γ) in alkane carbochlorides is higher than in reactions without a solvent. The effect of the solvent manifests itself remarkably in the chlorinations of propionyl chloride at low temperature. The phenomena observed can be explained as follows.

When the reaction is carried out without a solvent, β-chloropropionyl chloride is the chief product. Although C_β is a primary carbon atom, the activation energy of the abstraction of hydrogen from this atom (E_β) is lower than that from the secondary C_α(E_α), due to the greater electron availability at C_β. In carbon disulphide E_α is lower than E_β for in this case the resonance stabilized $H_3C - \dot{C}H - COCl$ radical is more important in the transition state. Thus, at -70° in an excess of carbon disulphide the secondary chloro derivative is the chief product.



Photochlorination of propionyl chloride

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