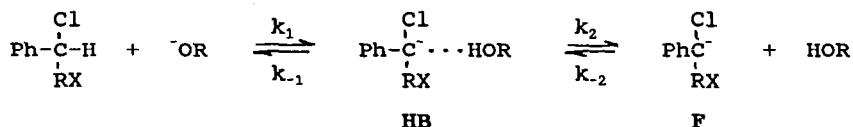


EFFECT OF BETA-FLUORIDE ON DEHYDROHALOGENATION REACTIONS

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A multi-step mechanism with two carbanions accounts for results of alkoxide-promoted dehydrohalogenation reactions:



Chloride leaves from a hydrogen-bonded carbanion, HB, regardless of the nature of RX: CF₂Cl, CHFCl or CH₂Cl. Fluoride leaving from CH₂F can depart from HB, while loss from CF₃ requires formation of the intermediate F, which is not stabilized by contact with either a gegen ion or solvent molecule.

Beta-fluoride increases rates of dehydrochlorination: CH₂Cl (1.0), CHFCl (6-25)¹ and CF₃ (175); however, the reverse is noted for loss of HF: CH₂F (1.0), CHF₂ (0.6) and CF₃ (0.05). In all cases observed isotope effects, $k^{\text{H}}/k^{\text{D}}$ at 25°C, decrease with added beta-fluorines: CH₂Cl (4.24), CHFCl (3.15) and CF₂Cl (3.02); CH₂F (2.16), CHF₂ (1.53) and CF₃ (1.08). The exchange of hydrogen from PhCHClCF₃ occurs ten times faster than loss of HF and results in a $k^{\text{H}}/k^{\text{D}} = 1.05$. This is consistent with loss of HF and the exchange reaction requiring the formation of F.

Element effects applied to dehydrohalogenation reactions usually refer to bromide vs. chloride. Results for our systems are about half of those reported for PhCH₂CH₂X, $k^{\text{Br}}/k^{\text{Cl}} = 79$: PhCHClCH₂X (35) and PhCHBrCF₂X (39); however, the chloride/fluoride element effect varies widely with PhCHClCH₂F, $k^{\text{Cl}}/k^{\text{F}} = 68$, the same as that reported for PhCH₂CH₂F, but increasing to 1×10^3 for PhCHClCHF₂¹ and 1.1×10^5 for PhCHClCF₃. The measurement of element effects should be ideal for a competition within the same molecule, >CH-CBrClF. Loss of fluoride can not compete with chloride or bromide in the systems cited above. Studies using PhC^HBrCFClBr result in large differences in $k^{\text{Br}}/k^{\text{Cl}}$ that depend on solvent, temperature or ¹H for one diastereomer, but not for the other.

¹The rate depends on the diastereomer.