(a) A is faster than B (S_N2 reaction, 1˚ LG > 2˚ LG)

(b) B is faster than A (S_N2 reaction, large atom more nucleophilic/polarizable nbe pr)

(c) B is faster than A (S_N1 reaction, 3˚ LG >> 1˚ LG to make a C+)

(d) B is faster than A (S_N2 reaction, I is a better LG than Br: larger atom = weaker bond)

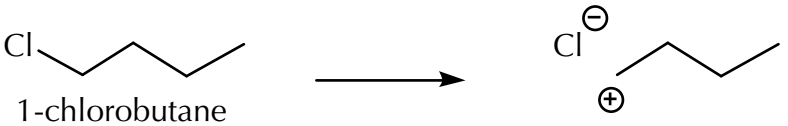
(e) A is faster than B (S_N2 reaction, polar aprotic solvent has no hydrogen bonding so the anion is more reactive than in water)

(f) A is faster than B (S_N2 reaction, nucleophilicity follows basicity/lower eN in a row)

(g) B is faster than A (S_N2 reaction, OTf is a better LG than the OMs group; the fluorine atoms weaken the CO bond/stabilize the O- of the LG)

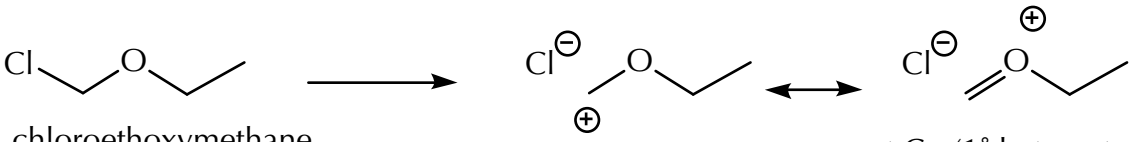
The statement "the observed unimolecular substitution rates" means that we are looking at the rate of formation of the carbocation, which is related to differences in stability between them. They are all 1° C+, and the reference compound (1-chlorobutane) would be expected to be quite slow in forming a carbocation (enough so that it is not predicted to occur in the absence of direct information, such as this).

The chloroethoxymethane gives a resonance-stabilized carbocation, so its reaction rate is exceptionally faster than the 1-chlorobutane. In the 1-chloro-2-methoxyethane case, the electron-withdrawing (inductive) effect of the electronegative oxygen makes is worse to form the positive charge of the carbocation, and so it is even slower than the already slow 1-chloropropane.



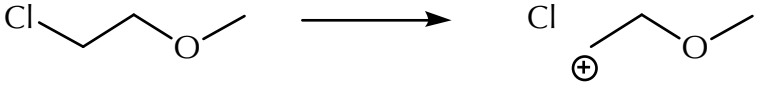
1-chlorobutane

poor C+ (1° C)



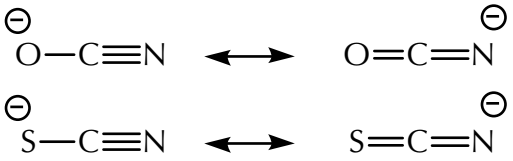
chloroethoxymethane
10^9 faster than
1-chlorobutane

great C+ (1° heteroatom)



1-chloro-2-methoxyethane
0.20 of the rate of
1-chlorobutane

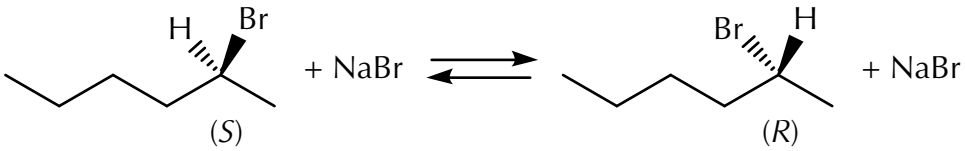
even poorer C+ (1° C with electron-withdrawing effect of the O atom)



Both ions have $\delta^{\ominus}$ at each end.

In a nitrogen versus oxygen comparison, the greater electronegativity of O over N (as seen in, e.g., ammonia versus water) reduced the nucleophilicity of the O atom relative to the N atom, resulting in the N-attached substitution product.

In the nitrogen versus sulfur comparison, however, the larger atom size of the third row S atom and its more polarizable electrons appears to win the competition with the N atom (it's also true that the electronegativity of S is less than that of N, almost exactly the same as C, so this might also be included as a contributing factor).



The (*S*)-2-bromopentane undergoes an S_N2 reaction with NaBr to form the (*R*)-2-bromopentane. The reaction creates the enantiomer. The reaction is reversible, and so an equilibrium is established between the enantiomers, which ends up being 1:1 because the ΔG° between them is 0 kcal/mol ($K_{EQ} = 1$). The resulting racemic mixture is optically inactive.

As a bimolecular reaction, increasing the concentration of NaBr will increase the reaction rate, causing the racemic mixture (and hence the optical inactivity) to be established more rapidly.