The magnitude of the positive charge of the reaction initiator and the selectivity

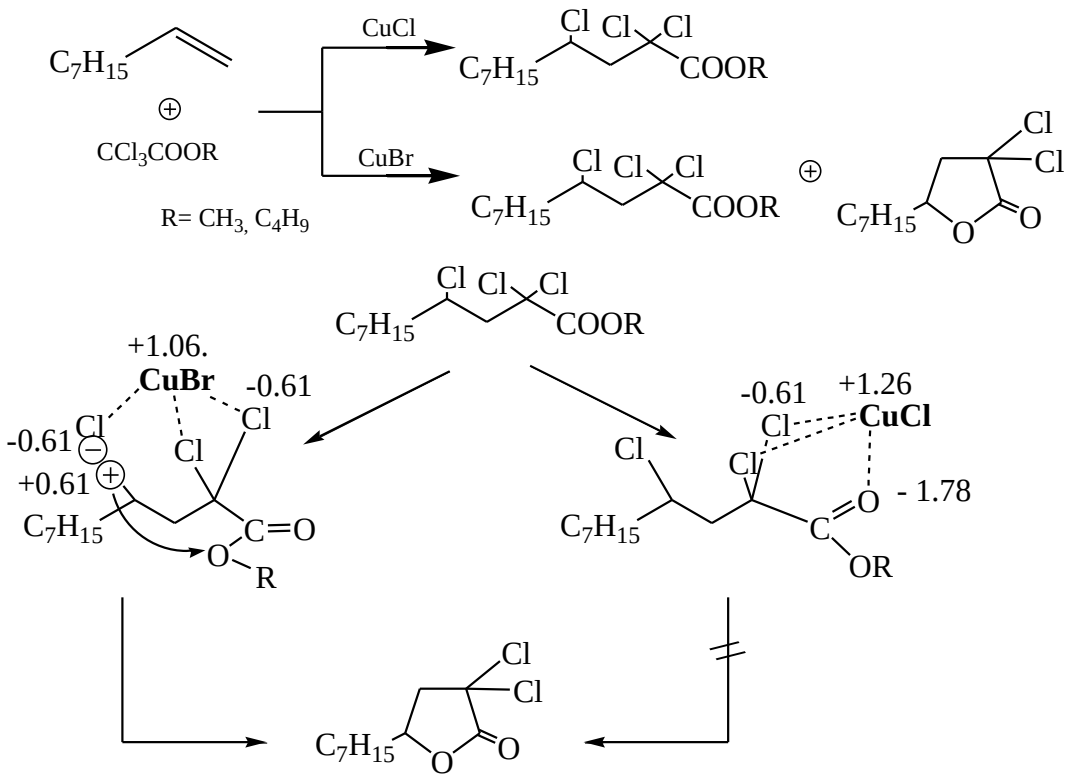
K.H. Petrosyan Yerevan State University petrosyankima@ysu.am

It was found by us that depending on the magnitude of the charge of copper an interesting phenomenon is observed: the activity of the reaction is being altered. This can be interpreted using the HSAB theory of Pearson [1]

The addition reaction of nonen-1 and alkyl trichloroacetates was investigated. It was shown that in the presence of copper chloride the only products of the reaction are the esters of 2,2,4-trichloroundecanoic acid, whereas the same reaction in the presence of cuprous monobromide leads to the mixture of the above mentioned esters and 2,2-dichlor-4-heptibutirolaktone in the proportion 1:9.[2] The elucidation of the origins of this chemoselectivity alteration is in progress.

The second compound has absorption of 1780см$^{-1}$ on IR spectrum, which is characteristic of butyrolactone moeity. We also showed that the proportion of the lactone increases as we allow the reaction to proceed for longer time periods (IR spectrum monitoring for the ratio of intensities of carbonyl groups).

The mechanism of the reaction is not known, but there is a hypothesis that it is a redox process that underlies it. Copper bromide with trichloride leads to the formation of lactone as a weaker Poling acid (charge strength +1.06) than copper chloride (charge strength +1.26),



X_{Cu} =1.9; X_{Br}=2.96; X_{Cl}=3.16 ; X_C=2.55; X_O=3.44; X_{C-Cl}=3.16-2.55=0.61. $AF(C)_{C-Cl}$= +0.61. $DF(Cl)_{C-Cl}$= -0.61. X_{C-O}=3.44-2.55=0.89. $AF(C)_{C=O}$= +0.89x2= +1.78. $DF(O)_{C=O}$= -0.89x2= - 1.78. X_{Cu-Cl}=3.16-1.90=1.26. $AF(Cu)_{Cu-Cl}$= +1.26. $DF(Cl)_{Cu-Cl}$= -1.26. X_{Cu-Br}=2.96-1.90=1.06. $AF(Cu)_{Cu-Br}$= +1.06. $DF(Br)_{Cu-Br}$= +1.06.

1. Reutov O.A., Kurz A.L., Butin K.P., Moscow 2005, part 1, p. 206

2. Petrosyan K.H. Arm Chem. Journal 2006, ch. 59, p. 138-143