

Forecasts of halogen reactivity under the light of acid-base theory

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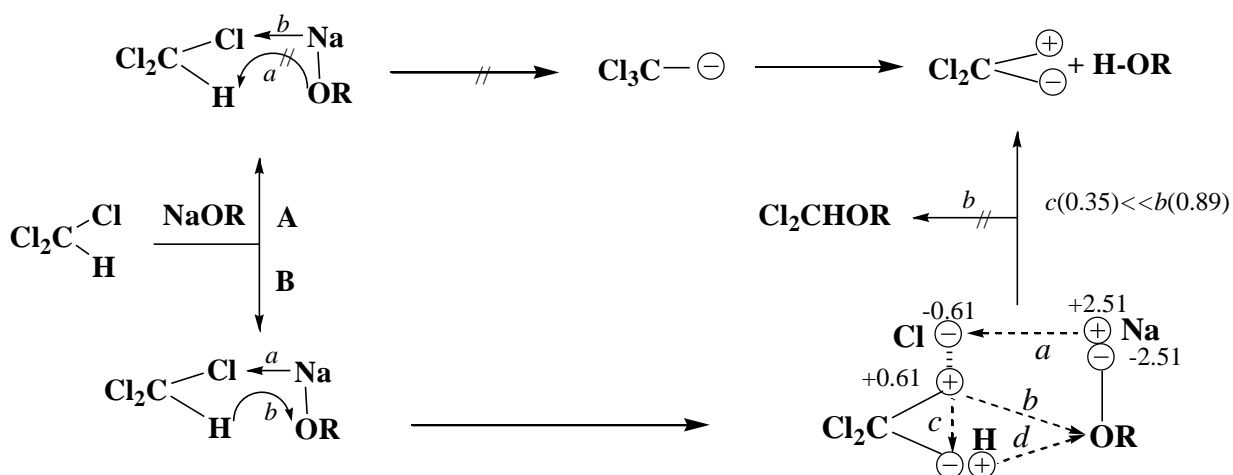
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In spite of classic theory it is shown that haloform(trihalogenmethans) interactions with bases is controlled not by movability of the hydrogen of C-H bond, but by heterolysis of the C-halogen bond. For that reason, our acid-base theory regards the order of haloform reactivities ($\text{CHF}_3 < \text{CHCl}_3 < \text{CHBr}_3 < \text{CHJ}_3$), which is experimentally observed, not as an anomaly but as a standard occurrence. According to some data, so-called α -elimination starts on the stage of deprotonation[1], while other data point to the dissociation of the C-Hal bond as the first step.[2,3]

In light of general theory of acids and bases all reactions are viewed as acid-base and red-ox. During the interaction of the molecules of haloform with the base (sodium alcoholate) the atom of hydrogen of that C-H acid cannot play the role of the initiator of the reaction. The reason is obvious: there is a stronger Lewis acid (Na charge strength + 2.51)[4] in the reaction mixture than the C-H (charge strength +0.35) acid. In such a competition only the sodium atom can become the initiator of the reaction. Thereby, the attack of such a particle is always directed towards the halogen if C-Hal of the haloform, but not the hydrogen of C-H. According to the general acid-base theory, reaction is proceeding in the direction where the charge barrier is being most easily passed; thus, in the direction C-F, C-Cl, C-Br, C-I, as the heterolysis of the bond becomes easier.

$$X_{\text{C-H}} = 2.55 - 2.20 = 0.35, \quad X_{\text{F-C}} = 3.98 - 2.55 = 1.43, \quad X_{\text{Cl-C}} = 3.16 - 2.55 = 0.61, \quad X_{\text{Br-C}} = 2.96 - 2.55 = 0.41,$$

$$X_{\text{J-C}} = 2.66 - 2.55 = 0.11, \quad X_{\text{O-Na}} = 3.44 - 0.93 = 2.51$$



1. Sykes P. A Guidebook to Mechanism in Organic Chemistry 1996 p.416
2. Nefedov O.M. Chemistry of Carbene's 1990, p.83-158
3. March J., Advanced Organic Chemistry 1994 p. 1495
4. Gevorkyan A.A., Petrosyan K.H. Arm Chem Journal 2006, 76, No7, 1223